# Corrosion

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## TECHNICAL SECTION

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## Nace News

## General News

## Technical Topics

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## SCHEDULED FOR PUBLICATION IN MAY

## Experience With Sweet Oil Well Tubing Coated Internally With Plastics

### A Status Report of NACE Technical Unit Committee T-1C on Sweet Oil Well Corrosion

Detailing reports on 419 wells in 38 fields in the Texas and Louisiana Gulf Coast area in which plastic coated tubing is used. Service periods up to 10 years are covered.

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**THIS MONTH'S COVER**—This view of a part of the 19-mile 4 and 6-inch 3003 alloy aluminum water pipeline connecting a river to a water-flooding operation in the Pembina oil field was taken before the pipe was buried bare. This is believed to be the longest unprotected buried aluminum pipeline so far installed in the world. Wall thickness is from 0.188 to 0.310-inch. (Photo: Aluminium Laboratories, Ltd., Kingston, Ont.)

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# Directory of NACE Regional and Sectional Officers

## CANADIAN REGION

B. H. Levelton, Chairman; B. C. Research Council, University of B. C., Vancouver 8, B. C., Canada.

H. G. Burbidge, Vice-Chairman; Aluminum Company of Canada, Ltd., 1700 Sun Life Building, Montreal, Quebec, Canada.

W. G. Brander, Secretary-Treasurer; Northwestern Utilities, Ltd., 10124 - 104th Street, Edmonton, Alberta, Canada.

A. R. Murdison, Director; Imperial Oil Ltd., Pipe Line Division, 111 St. Clair Avenue, West, Toronto, Ontario, Canada.

### • Calgary Section

D. S. McIntosh, Chairman; Britamoil Pipe Line Co. Ltd., P. O. Box 130, Calgary, Alberta, Canada

G. Mainland, Vice-Chairman; Imperial Oil Ltd., Tech. Serv. Lab., 300 - 9th Avenue, West, Calgary, Alberta, Canada

E. W. Abercrombie, Secretary-Treasurer; Aluminum Company of Canada, 118 - 5th Avenue, S. E. Calgary, Alberta, Canada

### • Edmonton Section

W. G. Brander, Chairman; Northwestern Utilities, Ltd., 10124 - 104th Street, Edmonton, Alberta, Canada

W. H. Seager, Vice-Chairman; Canadian Protective Coating Ltd., 9336 - 91st Street, Edmonton, Alberta, Canada

E. E. Moore, Secretary-Treasurer; Interprovincial Pipe Line Co., 10049 Jasper Avenue, Edmonton, Alberta, Canada

### • Hamilton-Niagara Section

H. W. Hyslop, Chairman; United Gas & Fuel Co., of Hamilton, Ltd., 82 King St. E., Hamilton, Ontario, Canada

### • Montreal Section

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### • Toronto Section

H. A. Webster, Chairman; Corrosion Service Ltd., 17 Dundonald Street, Toronto, Ontario, Canada

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Frank Farrer, Secretary-Treasurer; Trans-Northern Pipeline Co., Ltd., 696 Yonge Street, Toronto, Ontario, Canada

### • Vancouver Section

J. McLaughlin, Chairman; Industrial Coatings Ltd., 1920 Main Street, Vancouver 10, B. C., Canada

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## NORTH CENTRAL REGION

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W. E. Hare, Chairman; Hare Equipment Company, 1720 Section Road, Cincinnati 37, Ohio

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### • Chicago Section

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### • Cleveland Section

A. R. Corlett, Chairman; Harco Corp., P. O. Box 7026, Cleveland 28, Ohio

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### • Detroit Section

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Euel Vines, Treasurer; Koppers Company, Inc. 301 W. Eight Mile Road, Detroit, Mich.

### • Eastern Wisconsin Section

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### • Greater St. Louis Section

Charles W. Ambler, Chairman; American Zinc, Lead & Smelting Co., P. O. Box 495, East St. Louis, Illinois

Oliver W. Siebert, Vice-Chairman; Monsanto Chemical Company, W. G. Krummrich Plant, Monsanto, Illinois

Dean Jarboe, Secretary; Celucoat Corp., 6161 Maple Avenue, St. Louis 14, Missouri

A. O. Fisher, Treasurer; Engineering Dept., Monsanto Chemical Company, Lindbergh & Olive Streets, St. Louis, Missouri

### • Kansas City Section

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### • Southwestern Ohio Section

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## NORTHEAST REGION

Frank E. Costanzo, Director; 253 Ryan Drive, Pittsburgh 20, Pa.

Edward L. Simons, Chairman; General Electric Company, Research Laboratory, P. O. Box 1088, Schenectady, New York.

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### • Baltimore Section

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L. Andrew Kellogg, Vice-Chairman; Niagara Mohawk Power Corp., 300 Erie Boulevard West, Syracuse 2, N. Y.

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William H. Rutter, Secretary-Treasurer; Electro Chemical Eng. & Mfg. Co., 750 Broad Street, Emmaus, Pa.

### • Metropolitan New York Section

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# Directory of NACE Regional and Sectional Officers

(Continued From Page 6)

● **Pittsburgh Section**

A. B. McKee, Chairman; Alcoa Research Laboratories, Freeport Road, New Kensington, Pennsylvania

S. H. Kalin, Vice-Chairman; U. S. Steel Research Lab., Monroeville, Pennsylvania

R. W. Maier, Secretary; Gulf Oil Corp., 4th floor, Gulf Bldg., Pittsburgh 19, Pennsylvania

C. L. Dey, Treasurer; Koppers Company, Inc., Koppers Bldg., Pittsburgh 19, Pennsylvania

● **Schenectady-Albany-Troy Section**

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R. Clark, Vice-Chairman; Alco Products, Inc., 1 Nott Street, Schenectady, New York

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● **Southern New England Section**

E. A. Tice, Chairman; The International Nickel Company, 75 Pearl Street, Hartford, Conn.

Archer B. Hamilton, Vice-Chairman; The Hartford Gas Company, 233 Pearl, Hartford 4, Conn.

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## SOUTHEAST REGION

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● **East Tennessee Section**

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● **Jacksonville (Fla.) Section**

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● **Tidewater Section**

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## SOUTH CENTRAL REGION

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W. F. Levert, Secretary-Treasurer; United Gas Pipe Line Co., P. O. Box 1407, Shreveport, Louisiana

Dan H. Carpenter, Asst. Secretary-Treasurer; Aquaness Dept., Atlas Powder Company, P. O. Box 8521, Oklahoma City, Okla.

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● **Central Oklahoma Section**

R. V. James, Chairman; University of Oklahoma, Norman, Okla.

George Evans, Vice-Chairman; 2462 N. W. 37th Place, Oklahoma City 12, Okla.

Frank B. Burns, Secretary-Treasurer; Kerr McGee Oil Industries, Inc., P. O. Box 125, Wynnewood Okla.

C. C. Allen, Trustee; Anderson-Prichard Oil Corp., 1000 Liberty Bank Bldg., Oklahoma City 2, Okla.

● **Corpus Christi Section**

Kenneth R. Sims, Chairman; Gas Division, Department of Public Utilities, P. O. Box 111, Corpus Christi, Texas

William Taylor, Vice-Chairman; Gas Department, City of Corpus Christi, P. O. Box 1622, Corpus Christi, Texas

Joseph L. Willing, Jr., Secretary-Treasurer; Humble Pipe Line Company, P. O. Box 1051, Corpus Christi, Texas

John P. Westerveldt, Trustee; Pontiac Pipe Line & Export Co., P. O. Box 1581, Corpus Christi, Texas

● **East Texas Section**

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Gene E. Smith, Vice Chairman; 1012 Bledsoe Street, Gilmer, Texas

H. E. Schilling, Secretary; Sun Oil Company, P. O. Box 267, Carthage, Texas

Ike H. Hartsell, Treasurer; Tretolite Company, P. O. Box 1181, Gladewater, Texas

James C. Orchard, Trustee; Cardinal Chemical Company, P. O. Box 54, Longview, Texas

● **Greater Baton Rouge Area Temporary Officers**

P. E. Weaver, Chairman; Dow Chemical Company, Commerce Building, Baton Rouge, La.

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● **Houston Section**

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C. B. Tinsley, Secretary-Treasurer; Southwestern Bell Telephone Company, 1119 Capitol Avenue, Room 601, Houston 2, Texas

Charles L. Woody, Trustee; United Gas Corporation, P. O. Box 2628, Houston 2, Texas

● **New Orleans-Baton Rouge Section**

F. A. MacDougall, Chairman; Shell Oil Company, P. O. Box 193, New Orleans, La.

William L. Voorhies, Vice Chairman; Freeport Sulphur Company, Port Sulphur, La.

Keith Ebner, Sec.-Treas.; The Texas Company, P. O. Box 7, Harvey, La.

O. L. Grosz, Trustee; The California Company, P. O. Box 128, Harvey, La.

● **North Texas Section**

Glyn Beesley, Chairman; Dallas Power & Light Company, 1506 Commerce Street, Dallas, Texas

E. J. Simmons, Vice Chairman; Sun Oil Company, P. O. Box 2880, Dallas, Texas.

Don Taylor, Sec.-Treas.; Otis Pressure Control, Inc., P. O. Box 35206, Dallas, Texas.

Howard Greenwell, Trustee; Production Profits, Inc., 8912 Sovereign Row, Dallas, Texas.

● **Panhandle Section**

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James W. Edminster, Secretary-Treasurer; Cabot Carbon Company, P. O. Box 1101, Pampa, Texas

● **Permian Basin Section**

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● **Rocky Mountain Section**

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● **Sabine-Neches Section**

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● **Shreveport Section**

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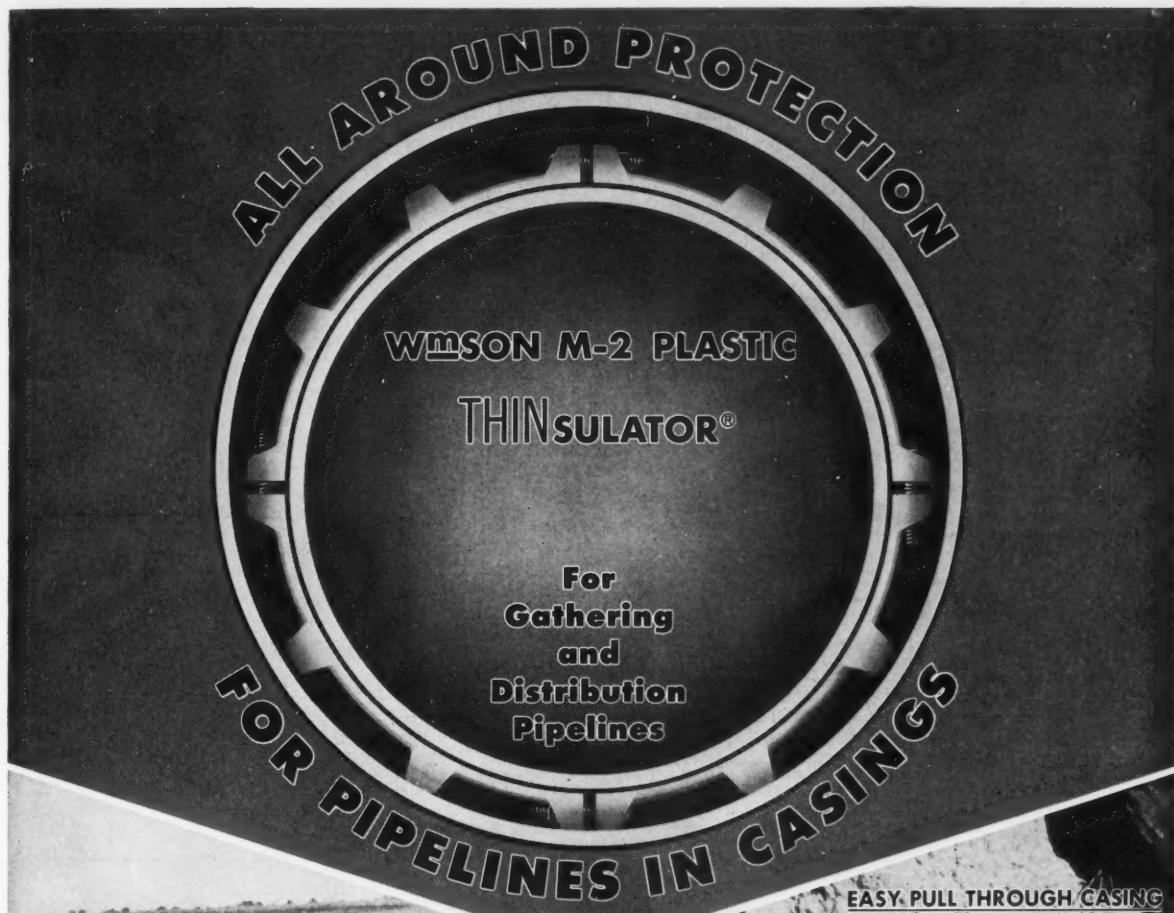
# Directory of NACE Regional and Sectional Officers

(Continued From Page 8)

● **Teche Section**

Max I. Suchanek, Chairman; District Product Engineer, Dowell, Inc., P. O. Box 830, Lafayette, La.

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● **Tulsa Section**

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Parke D. Muir, Secretary; Dowell, Inc., Box 536, Tulsa, Okla.

Roger J. Norris, Treasurer; Koppers Company, Inc., 310 Thompson Building, 20 E. Fifth Street, Tulsa, Okla.
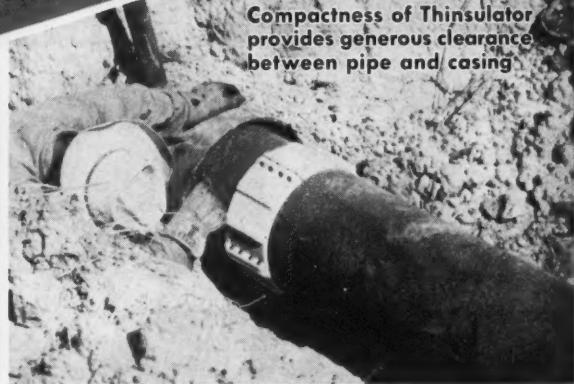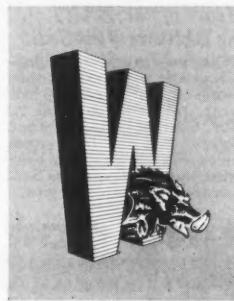
T. D. Williamson, Jr., Trustee; T. D. Williamson, Inc., P. O. Box 4038, Tulsa 9, Oklahoma

● **West Kansas Section**

G. H. Fanshier, Chairman; Corrosion Rectifying Company, R. R. 2, Great Bend, Kansas.

Roy Junkins, Vice Chairman; Cities Service Oil Company, 1613 N. Main, Great Bend, Kansas.

Ray Walsh, Sec.-Treas.; Aquaness Dept., Atlas Powder Company, 1230 Grant Street, Great Bend, Kansas.

W. C. Koger, Trustee; Cities Service Oil Company, Cities Service Building, Bartlesville, Okla.

## WESTERN REGION

E. H. Tandy, Director; Standard Oil Company of California, P. O. Box 97, El Segundo, Cal.

E. F. Bladholm, Chairman; Southern California Edison Co., 601 W. 5th Street, Los Angeles, Cal.

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C. M. Schillmoller, Secretary-Treasurer; The International Nickel Company, Inc., West Coast Technical Section, 538 Petroleum Bldg., Los Angeles 15, Cal.

● **Central Arizona Section**

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Russell Jackson, Vice-Chairman, Rust-Proofing, Inc., P. O. Box 1671, Phoenix, Ariz.

Roy P. Osborn, Secretary-Treasurer; Mountain State Tel. & Tel. Company, Box 2320, Phoenix, Arizona

● **Los Angeles Section**

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● **Puget Sound Section**

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Norman H. Burnett, Vice-Chairman; 230 South 187th Street, Seattle 88, Wash.

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● **Salt Lake Section**

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Frank L. Pehrson, Secretary-Treasurer: Kennecott Copper Corp., P. O. Box 1650, Salt Lake City, Utah

● **San Diego Section**

L. L. Flor, Chairman; 1036 Leslie Road, El Cajon, Cal.

Kenneth R. Christy, Vice Chairman; Federal Housing Administration, 601 "A" Street, Room 201, San Diego 1, Cal.

Reuben C. Tullis, Secretary-Treasurer; 543 Gala Avenue, San Diego 15, Cal.

● **San Joaquin Valley Section**

Robert L. Davis, Chairman; The Superior Oil Co., P. O. Box 1031, Bakersfield, Cal.

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● **San Francisco Bay Area Section**

J. B. Dotson, Chairman; Rockwell Mfg. Co., Nordstrom Valve Div., 2431 Peralta Street, Oakland, Cal.

J. P. Fraser, Vice Chairman; 39 Claremont Drive, Orinda, Cal.

B. A. Kronmiller, Secretary-Treasurer; The Flox Co. Inc., P. O. Box 296, Alameda, Cal.

## Technical Articles Scheduled For May

On the Mechanism of Stress Corrosion of Austenitic Stainless Steels in Hot Aqueous Chloride Solutions by K. W. Leu and J. N. Helle

Thin Metal Film Corrosion Indicators by David Roller

Corrosion and the Destination of Corrosion Products in High Pressure Power Plant by Ross C. Tucker

Microbiological Deterioration of Buried Pipe and Cable Coatings by F. E. Kulman

Corrosion Problems in Water Flooding by Ray W. Amstutz

Electrical Measurements and Their Interpretation in Underground Cable Corrosion Problems by K. G. Compton

Effects of Cold Working on Corrosion of High Purity Aluminum in Water at High Temperatures by M. J. Lavigne

Means of Increasing Corrosion Resistance of Metal Alloys by N. D. Tomashov

Corrosion of Zinc by Differential Aeration by G. Bianchi

# THE NATIONAL ASSOCIATION OF CORROSION ENGINEERS

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Topic of the Month

# The Motor Coach and Aluminum

### By LEONARD C. ROWE*

## Introduction

THE MOTOR Coach Industry presents an enviable testimonial for the use of aluminum in transportation vehicles. The first all-aluminum body was constructed in the year 1930. Thus, the transportation industry has had more than a quarter century in which to field-test aluminum for corrosion resistance. As other road type vehicles move into an expanded usage of aluminum, it might be well for these manufacturers to cast a glance at the old pros for a few hints.

The modern coach utilizes aluminum as its primary metal of construction. Aluminum accounts for 50 percent of the total body weight and 23 percent of the overall vehicle weight. This represents some 4500 pounds of aluminum per vehicle. The use of aluminum was first initiated as a dollar and cents proposition. In order to be licensed a coach is restricted to a loaded weight of 18,000 pounds per axle. The use of a light metal enables a larger coach to be built which will accommodate more passengers.

## Durability Requirements

Durability and corrosion resistance are musts in coach construction. City coaches are built with an expected minimum life of ten years. This represents close to one-half million road miles. Inter-city coaches are expected to give a fifteen year life and about two and one-half million road miles. In each year of service, coaches are exposed to the full gamut of variable weather conditions and corrosive city air contaminants. Although high humidity conditions are properly controlled by air conditioning on the interior, a highly moistened air is available to some of the interior metals. Under such adverse exposure conditions, it is understandable that metals must be used that represent maximum corrosion resistance.

The excellent corrosion resistance received from aluminum in coach construction is based upon experience and the proper application of corrosion fundamentals. This approach has lead to

an expert choice of alloys and adequate protective treatments. Type 5052 aluminum sheet is used for body and roof panels. Type 6062 and 6063 extrusions are used in cross members where structural strength and appearance are desired. Many cast aluminum alloys are used in other coach components, depending upon the desired characteristics and treatment. Aluminum has even been used for front and rear bumpers of inter-city coaches for some ten years.

## Corrosion Problems

Aluminum has not always registered complete corrosion resistance. A typical problem was the persistent corrosion that was experienced in the use of cast aluminum water outlet manifolds bolted to cast iron cylinder heads. Figure 1 shows the extent of corrosion of an aluminum manifold after 130,000 miles. A pitting type of corrosion occurred at the intake ports. Corrosion progressed sufficiently at ports 1 and 6 to cause leakage through the bolt holes.
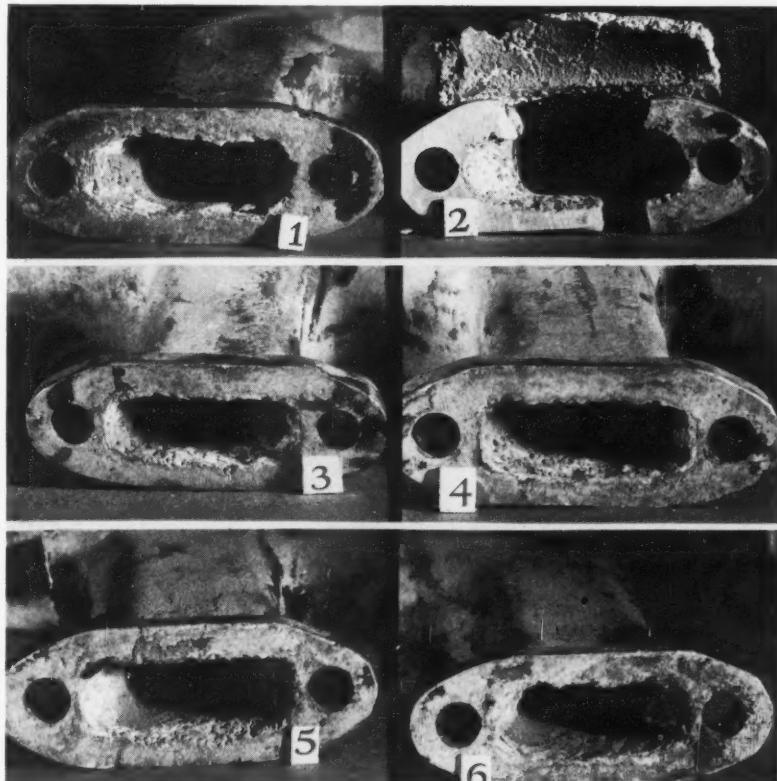


Figure 1—Advanced corrosion of cast aluminum water outlet manifold used with cast iron cylinder head.

* Research Staff, General Motors Corp., Detroit, Michigan.

Field tests were conducted in an attempt to stifle the corrosion. Preventives consisted of the use of specific coatings for aluminum and the controlled use of soluble oil as an inhibitor in the coolant. It was found that the soluble oil inhibitor eliminated the corrosion problem to the extent that operators could get satisfactory life from the coach without extensive overhauling and replacement of parts.

A more recent move is the complete use of aluminum for both manifolds and cylinder heads. This has alleviated the galvanic cell between the cast iron and aluminum, thus going directly to the seat of the trouble.

The continual willingness of the motor coach industry to take a problem and successfully make corrective measures has enabled them to make greater use of aluminum metal. In most cases, however, protective measures have been taken before trouble occurs. Where bright aluminum is desired, it is anodized. Surfaces to be painted receive a proprietary phosphate treatment followed by a zinc chromate primer and an enamel finish coat. The rigors of galvanic corrosion are avoided whenever possible although aluminum and stainless steel have been used together without noticeable effect. The junctures between aluminum and plain steel have given trouble when only a prime coat was used on the steel. This was remedied by giving a more protective coating to the cathodic metal (steel in this case.) A zinc chromate caulking compound is used between aluminum panels and steel body posts. In a few cases, such as the battery carrier, the natural resistance of aluminum to battery acid has proven satisfactory and more economical than using acid-proof coatings over other metals.

The manufacturer can provide the basic know-how of construction and protection, but experience has taught that the operator must practice good maintenance procedure. A well drained and clean understructure is a simple deterent to extensive underbody corrosion. A clean coach means not only a better appearing one but also extended life through less corrosion.

# Cathodic Protection of Lead Cable Sheath
# In the Presence of Alkali from Deicing Salts*

## By WALTER H. BRUCKNER and W. W. LICHTENBERGER

## Introduction

THE CORROSION and failure of lead cable sheathing in an environment of deicing salts and under cathodic protection conditions is sufficiently well known to the power and communications industries to make welcome any advance in controls to prevent such failures. A previous paper on this subject by Bruckner and Wainwright[1] gave data showing that lead cable sheath could be completely protected cathodically at sufficiently high potential with a constant current source even in the presence of high pH and salt concentration. It also was indicated in the paper cited above that the corrosion experienced in service in the cathodic protection of lead was due only to failure to provide adequate and continuous cathodic protection. It remained then to determine under what conditions this level of cathodic protection could be provided in the varied service environment of lead cable sheath.

This paper presents the results of a study of lead cathodes in contact with electrolytes such as might be found in heavily salted duct or soil areas due to high concentration of deicing salt. The relationship of the potential of lead to salt concentration and to the high pH established as a consequence of cathodic protection and presence of salt were the prime objects of the research program.

## Experimental Procedure

It was considered desirable to establish initially the relationship of salt concentration to the potential of a lead cathode at various current densities. Accordingly, cells were arranged to have a section of ⅞-inch OD lead sheathed ground cable act as cathode in an electrolyte of aqueous salt solution; the cells also were provided with a number of graphite anodes concentric with the cathode. The glass jars used for the cells were about 9 inches ID and 12 inches high. A series of tests was made with NaCl in the electrolyte in the following concentrations: 100, 1,000, 10,000 and 50,000 ppm. Another series of tests was made with CaCl₂ in the same concentrations.

First of all, static potentials in the salt solutions were determined using a Piontelli-type probe pressed against the lead cathode. A constant current was introduced into the cell to make the cathode negative with respect to the solution, and the cathode potential versus time was recorded automatically on a Leeds and Northrup recorder over a 24 hour period. Upon terminating the

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**W. W. LICHTENBERGER** is instructor in electrical engineering at the University of Illinois where formerly he served as a research assistant in the Cathodic Protection Laboratory. He received a BS in electrical engineering in 1955 from the University of Illinois and an MS in 1956. He designed and built much of the equipment in the cathodic protection laboratory and has specialized in electronics and circuits. He has received several honors in recognition of his work at the university.

test the cathode was removed from the cell and the surface cleaned by immersion in chloracetic acid. After the cleaned surface was thoroughly washed with water, the cathode was replaced in the electrolyte for a redetermination of the static potential. When the static potential was the same as that obtained at the start of the previous run, current was again introduced into the cell at a higher current density than for the previous run.

The above tests were made in sequence at current densities of 1, 2, 5, 10, 20, 30, 40, 50, 75 and 100 ma per square foot. The data taken from the recorder chart provided a large number of curves for the relationship of potential to salt concentration and current density. Assembly of the data indicated no trend characteristic of anion, cation or salt concentration used in the polarization experiments. Furthermore, major inconsistencies were found in the data with respect to salt concentration as will be shown later in the section on data obtained. The only consistency which was obvious from the curves was that between 20 and 30 ma/ft² a dis-

## Abstract

It had been shown previously that complete protection of sheath could be effected in a constant current system even in the presence of high salt content and pH. The relationship of protective potentials to pH and salt concentration has now been established for commercial lead sheath alloy composition and is shown to be substantially the same as given in the Pourbaix diagram for pure lead.

The use of a potential gradient for lead cathodes was developed to provide simulated duct tests. The data from the gradient tests provided information on the effects of salt concentration, pH and potential on the corrosion behaviorism of lead when fully immersed and partially immersed. The criteria for effective cathodic protection are shown to be different for the portions of the lead cathode below, at and above the water line. The most severe corrosion conditions at the air-solution interface require a more negative voltage for protection than below the interface. The distribution of potential along the gradient as a function of salt content, type of salt and current input to the cell shows some important aspects to be considered in the field as possible regions of corrosion hazard. 7.7

continuous decrease in potential (more negative) regardless of the type of salt or concentration was in evidence.

The results of the initial polarization tests indicated that the potential established by a cathodic protection system on lead-sheathed cable operating in a salt electrolyte is governed by the pH established at the cathode surface at a definite current density. The next objective was to obtain polarization data on lead cathodes under conditions of known and constant pH at the lead surface. It was considered possible under the above conditions to check the polarization diagram for pure lead established by Delahay, Pourbaix and Van Rysselberghe.[2] The ultimate objective in making the check with the published polarization diagram for pure lead was to find how closely the relationship of potential to corrosion behavior of pure lead followed that for the alloys of lead used for power cable sheathing.

The potential pH tests were made in a specially constructed miniature cell which permitted the use of lead foil for the anode and cathode elements. The foil was rolled to a thickness of 0.005-inch from sections taken from a 1⅞-inch OD lead cable sheath. The use of lead foil made it possible to have a standard, reproducible surface for the cathodic potential measurements. Moreover, replacement of an electrode merely involved removing a small section of foil and replacing with a new section. An expanded view of the cell structure is shown in Figure 1. In operation the cell had the appearance shown in Figure 2, which shows the Piontelli-type probe at the right side next to the cathode.

The electrolyte used was made by
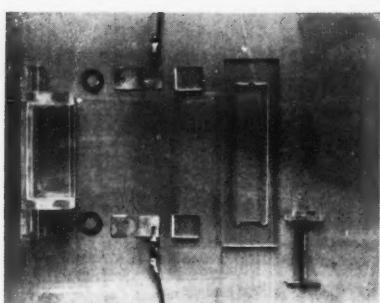
Figure 1—Miniature cell, expanded view.
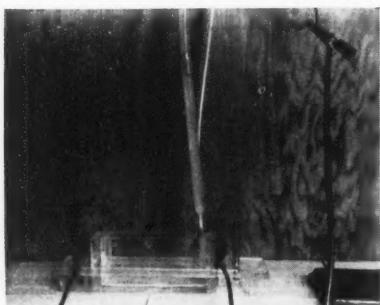

Figure 2—Miniature cell, assembled.


Figure 3—Polarization of lead in CaCl₂ solution (10,000 ppm).
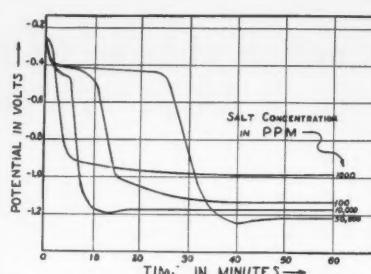

Figure 4—Polarization of lead in NaCl solution at 75 ma/sq. ft.


Figure 5—Cathode polarization of lead in NaCl solution.


Figure 6—Cathode polarization of lead in CaCl₂ solution.
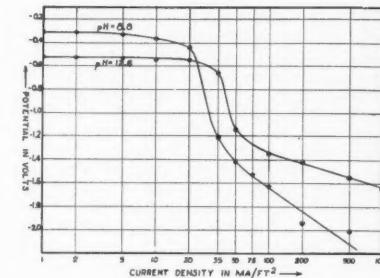

Figure 7—Potential versus current density for constant pH.

adding enough NaOH to a solution of 100 ppm NaCl in demineralized water to give the initial pH desired. It was considered that two different polarization tests (i.e., one with a pH of about 8.5 and another at a pH of about 12.6), would be sufficient to determine tentatively the applicability of the "Pourbaix curves" of pure lead to the corrosion behavior of commercial lead sheath alloy.

In making the polarization tests with the miniature cell it was necessary that the cathode surface film be constantly stirred with a vigorous stream of nitrogen gas bubbles in order to prevent an increase in pH at the cathode. It was necessary to make the test of short duration in order to keep the rise of pH of the cell solution to a minimum value. When the above precautions were observed, remarkably consistent data were obtained over a range of current density from 1 to 500 ma per square foot. The data are presented later in the paper.

A final series of tests was made using a different experimental procedure known as "gradient testing." The cathode was initially a section of lead-sheathed ground cable ⅞-inch OD. The

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section was about four feet long and was provided with a soldered copper lead wire at one end. "Scotchrap" vinyl tape was used on both ends of the cable and the lead wire to prevent contact with the electrolyte. A 41-inch length of the cable surface was exposed as cathode when placed in a horizontal position in a lucite tube cell which, itself, was 52 inches long. The ends of the lucite tube were closed by means of lucite plates cemented in place. Thus it was possible to place the cable section in the tube with any desired depth of electrolyte. The use of a large amount of electrolyte could then provide cathodic protection under fully immersed conditions and reducing the amount would provide partial immersion conditions.

The purpose in establishing the gradient tests was to simulate conditions out in the field where either due to heavy localized salting or duct position a potential gradient exists in the cathodic protection installation. In order to establish a potential gradient in the cells, current was brought into the end of the cell opposite from that to which copper lead wire was attached. This was done with a salt bridge which made contact at one end with the electrolyte in the cell and at the other end with the electrolyte contained in a beaker placed close to the cell. A lead anode placed in the electrolyte contained in the beaker completed the circuit. This arrangement made it possible to apply current to the cathode without contamination of the catholyte with the anolyte.

The gradient test arrangement also made it possible to study the effects of salt concentration and polarization on current distribution and the effects of pH change in relation to level of cathodic protection. Observations were made on the corrosion behavior of the cathode in different regions of the potential gradient. The results of the tests

and their correlation with the other data presented in the paper are given in the discussion of results.

## Data Obtained

The types of data obtained from tests at different current densities and salt concentrations are shown by the samples given in Figures 3 and 4. The curves of Figure 3 show the characteristic decrease in absolute potential between 20 and 30 ma/feet.³ Figure 4 shows that no consistent relationship of potential and salt concentration is evident. The semi-log plots of potential versus current density for different concentrations of salt are given in Figures 5 and 6. The latter curves show either one or two discontinuities per curve for which no consistent relationship can be discovered either with salt concentration or current density.

The data obtained from the two series of tests at constant pH are given in Tables 1 and 2 in the curves of Figure 7. The tables show that the potentials at different current densities were established at reasonably constant values of pH. The curves show values of static potential and potential-current density values which are consistent with the known corrosion behavior of lead. The relationship of the data for constant pH to the values of the Pourbaix curve in the literature is discussed later in the paper.

A considerable amount of data have been assembled in the gradient tests to show the effects of operation of a cathodic protection system on lead cable in different salt and pH environment and under conditions of minimum and excessive current densities. The effects of salt concentration at low current density can be seen most clearly in the curves of Figures 8, 9, and 10. The curves show the potential-time relationship for three different concentrations of NaCl. Each separate curve in these figures represents a different distance
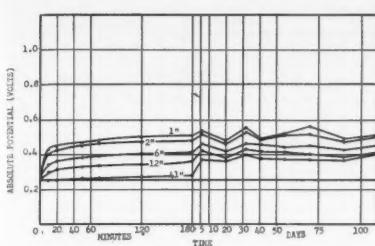
Figure 8—Potential time relationship for gradient test cathode with current of 3 ma and 10,000 ppm NaCl.
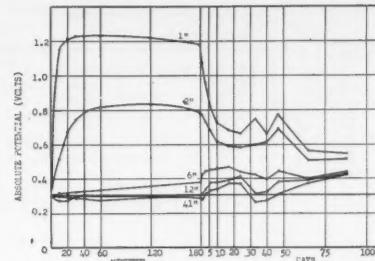


Figure 10—Potential time relationship for gradient test cathode with current of 3 ma and 100 ppm NaCl.
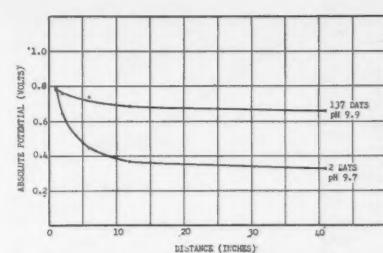


Figure 12—Potential gradient in cell with 3 ma and 10,000 ppm NaCl.
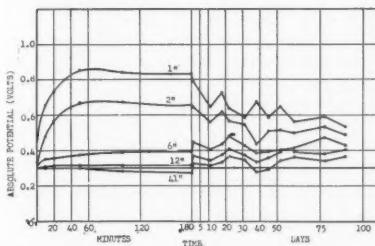


Figure 9—Potential time relationship for gradient test cathode with current of 3 ma and 1,000 ppm NaCl.
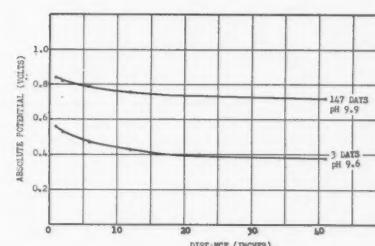


Figure 11—Potential gradient in cell with 3 ma and 10,000 ppm NaCl.
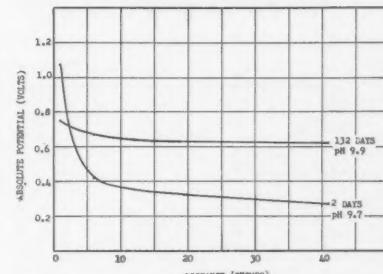


Figure 13—Potential gradient in cell with 3 ma and 100 ppm NaCl.

along the gradient from the point where current is introduced to the cell. The changes in the potential gradient due to differing conductivity of electrolyte are obvious from inspection of the curves. The effect of the potential or current density gradient on the pH is not obvious from the above curves since the pH is dependent not only on the current density but also on the speed with which the regions of high and low pH inter-diffuse along the horizontal lucite cell.

Figures 11, 12, and 13 show the stable potential at fixed time intervals over the entire distance of the potential gradient. The three sets of curves are respectively for salt concentration of 10,000, 1,000, and 100 ppm, and the time interval and pH range have been noted for each curve. By reference to the Pourbaix diagram for lead it is possible to determine the extent of cathodic protection provided in each region of the gradient. A discussion of the level of cathodic protection attained along the gradients shown in the above figures is given later in the paper.

## Discussion of Data

The form of the curves in Figure 3 indicates that for the particular application shown it was possible to establish a stable, polarized potential on the lead cable sheath at a current density between 20 and 30 ma per sq. ft. The discontinuity in the curves for current densities greater than 30 ma per sq. ft. is undoubtedly associated with considerable evolution of hydrogen from the cathode and the consequent increase in pH at or near the cathode. The increase in the value of the stable, polarized potential with increasing current density therefore would be expected to be associated with increasing pH at the cathode. However, the increasing evolution of hydrogen at higher current density would tend to aid in the dispersal of a film of high pH at the cathode and cause it to diffuse to re-

gions more remote from the cathode surface. Pourbaix and Van Muylder[3] show that under stagnant conditions the pH of the lead cathode film may go to values between 11 and 13. But, under dynamic conditions the pH is lower in relation to the current density than for a stagnant test.

### Determination of pH of Cathode Film

The pH of the cathode film under stagnant conditions is difficult if not impossible to determine; thus, Pourbaix and Van Muylder arrived at its value from dynamic tests. Their method was

to circulate electrolytes of successively higher pH until the potential was the same as that of the cathode film under stagnant conditions.

Since the initial polarization tests made with various concentrations of NaCl and CaCl₂ and with different current densities gave no indication of the cathode film pH corresponding to the potential at a definite current density, it was necessary to use a dynamic system under constant, known pH. The dynamic conditions were established by directing a stream of nitrogen bubbles at the lead cathode during the tests made in the miniature cell and the known pH was established as the initial condition of the cell electrolyte. The necessity of this

**TABLE 1—Polarization Data of Lead Cable Sheath Alloy as Cathode in 100 ppm NaCl with NaOH Added to Give pH Values, Shown.***

| Current Density (ma/sq ft) | Measured Potential (Volts) | Absolute Potential (H₂ =0) | pH (at end of run) |
|---|---|---|---|
| 0 | —0.547 | —0.305 | 8.7 |
| 1.0 | —0.549 | —0.307 | 8.55 |
| 0 | —0.546 | —0.304 | 8.7 |
| 2.0 | —0.552 | —0.310 | 8.7 |
| 0 | —0.542 | —0.300 | 8.7 |
| 5.0 | —0.568 | —0.326 | 8.6 |
| 0 | —0.544 | —0.302 | 8.9 |
| 10 | —0.610 | —0.368 | 8.9 |
| 0 | —0.546 | —0.304 | 8.9 |
| 20 | —0.670 | —0.428 | 8.9 |
| 0 | —0.547 | —0.305 | 8.9 |
| 35 | —1.455 | —1.213 | 8.9 |
| 0 | —0.546 | —0.304 | 8.9 |
| 50 | —1.657 | —1.415 | 8.7 |
| 0 | —0.565 | —0.323 | 8.9 |
| 75 | —1.778 | —1.536 | 8.7 |
| 0 | —0.572 | —0.330 | 9.0 |
| 100 | —1.868 | —1.626 | 9.0 |
| 0 | —0.584 | —0.342 | 9.0 |
| 200 | —2.177 | —1.935 | 9.1 |
| 0 | —0.585 | —0.343 | 9.1 |
| 500 | —2.330 | —2.088 | 9.7 Solution turned cloudy |

*Initial resistivity of electrolyte was 5000 Ω /cm³

**TABLE 2—Polarization Data of Lead Cable Sheath Alloy as Cathode in 100 ppm NaCl with NaOH Added to Give pH Values, Shown.***

| Current Density | Measured Potential | Absolute Potential (H₂ =0) | pH (at end of run) |
|---|---|---|---|
| 0 | —0.764 | —0.522 | 12.4 |
| 1.0 | —0.766 | —0.524 | 12.4 |
| 0 | —0.764 | —.522 | 12.4 |
| 2.0 | —0.767 | —0.525 | 12.4 |
| 0 | —0.763 | —0.521 | 12.4 |
| 5.0 | —0.768 | —0.526 | 12.4 |
| 0 | —0.763 | —0.521 | 12.4 |
| 10 | —0.772 | —0.530 | 12.4 |
| 0 | —0.762 | —0.520 | 12.4 |
| 20 | —0.785 | —0.543 | 12.4 |
| 0 | —0.762 | —0.520 | 12.4 |
| 35 | —0.899 | —0.657 | 12.4 |
| 0 | —0.760 | —0.518 | 12.4 |
| 50 | —1.389 | —1.147 | 12.5 |
| 0 | —0.760 | —0.518 | 12.5 |
| 100 | —1.582 | —1.340 | 12.5 |
| 0 | —0.759 | —0.517 | 12.5 |
| 200 | —1.661 | —1.419 | 12.6 |
| 0 | —0.762 | —0.520 | 12.6 |
| 500 | —1.784 | —1.542 | 12.6 |
| 0 | —0.769 | —0.527 | 12.6 |
| 1000 | —1.882 | —1.640 | 12.6 |

* Initial resistivity of electrolyte was 5000 Ω /cm³

Figure 14—Pourbaix diagrams of potential (H₂ = 0.0) versus pH for pure lead.



Figure 15—Schematic illustration of gradient test cell.

technique for determining the potential-pH relationship points up the observation that under cathodic protection of lead cable sheath, the pH of the electrolyte surrounding the cable need not be the same as that of the cathode film. In fact, if a colorimetric pH indicator is added to the cathodic protection cell the color is always more intense at the lead cathode than in the bulk of the electrolyte.

The two curves obtained for a constant pH of 8.8 and 12.6 respectively, shown in Figure 7, indicate that the protective potentials of —0.30 and —0.59 volts (absolute) for the respective pH value which are predicted by the Pourbaix diagram are obtained. In addition, the potential at which molecular hydrogen is discharged from the surface of the lead cathode at these pH values is —0.58 and —0.79 volts (absolute) as predicted from the Pourbaix curve, which is reproduced in Figure 14. It is seen from the curves that these values correspond to the most rapid rate of change of the slopes of the two curves.

It is apparent from the above data that the Pourbaix diagram for pure lead is most useful in predicting the potential required to establish an equilibrium relation between the lead surface and its environment at any pH. If the predicted potential is established and maintained without a change in the pH of the environment, a lead cathode uniformly so protected should provide a permanent installation free from any probability of failure. The Pourbaix diagram indicates that the only way for such a system to suffer corrosion damage would be to increase the pH, potential remaining constant, or to decrease

the potential, pH remaining constant. Both of the above possibilities could exist in service where potential gradients are found on the cathodically protected lead cable sheath. In the gradient, the region of high potential may be adequately protected, but due to the high current density a rapid build up of alkaline products is occasioned.

If there is little chance for diffusion away from the high current density areas the pH may build up to such high values that the established potential is no longer protective. If considerable diffusion occurs the high current density area may remain at sufficiently low pH to give protection; however, the diffusion of alkaline products to regions of lower potential in the potential gradient may give rise to corrosion problems.

### Gradient Tests

The gradient tests were initiated to survey some of the above problems as they might be presented in service. The potential gradient established in service may be a function of a number of variables including relative position of anodes with respect to the cathode, duct joints, soil resistance, current, and salt type and content in the electrolyte surrounding the cathode. A systematic survey of the many variables was initiated by use of a constant length of lead cathode, a constant current, and by varying the salt concentration and type of the electrolyte. The gradient test design has gone through a series of evolutionary changes and is now being carried out in the manner shown schematically in Figure 15.

Figure 15 shows the salt bridge at point A at the end of the long cell opposite to point B at which the current is brought out of the cathode. The cathode is about 40 inches long, 1¾ inches wide and 0.010 inches thick. As shown in Figure 15 the lead foil used as cathode is placed in the cell with the 1¾ inch width vertically disposed and immersed to half its depth in the cell electrolyte. It is seen that in such a cell the protective potential and current density will be a maximum at point A and will decrease to a minium value at B. The level of cathodic protection at any part of the cathode in such a cell will be dependent upon the pH and the potential established at any point. Close

observation of many such cells during initial polarization and subsequent operation for periods of several months indicates that the potential gradient becomes stabilized in a period of one or two days of operation. It indicates also that the pH rises to a maximum value in two days and becomes uniform throughout the length of the cell if the concentration of calcium ions in the electrolyte is at a low level.

Periodic observations are made of the potentials at various points of the cathode between points A and B; pH measurements also are made, and the cathodes are removed from the cells at intervals of two weeks to inspect them for the progress of any corrosion or pitting behavior in the areas below, at, and above the water line of the cell electrolyte. The relationship of any observed corrosion or pitting to the potential and pH can be determined by reference to the gradient measured.

At the time this paper was written (i.e., in June, 1957) there were seven gradient tests underway in the laboratory. Three of the cells operated with a current of 3 ma and with an electrolyte of NaCl in demineralized water. The pH of such cells became stabilized at around 9.5 with only slight variation along the cell length. The three above cells operated with different concentrations of NaCl in the range of 100, and 1,000, and 10,000 ppm.

Three other cells operated under the same conditions, except with CaCl₂, in the same concentration range. For the latter cells the pH tends to be higher at the high current density region of the gradient. Precipitation of basic calcium salts in the region of high pH prevents the diffusion of OH ions to the low potential region of the gradient. The gradient of pH from point A to B of the cell is a function of the concentration of calcium ions in the electrolyte; thus the behavior of a cathodic protection system in service also would be expected to depend upon both the type and concentration of the ions in the electrolyte.

### Colored Corrosion Products

The seventh cell used was the same as the six previously described except that the electrolyte was a mixture of

**TABLE 3—Expected Behavior of Lead Sheath Cathodically Protected Under a Potential Gradient.***

| Case No. | Current Input | Salt Content of Duct Solution | pH Established in Duct | CATHODIC PROTECTION CONDITIONS | |
|---|---|---|---|---|---|
| | | | | At Current Entry Region | Remote from Current Entry Region |
| 1. | Low | Low | Low | Slight overprotection | Slight corrosion tendency |
| 2. | High | Low | High | Excessive overprotection | Medium to severe corrosion |
| 3. | Low | High | Low | Uniform current distribution and possibly complete protection along gradient or slight general corrosion | |
| 4. | High | High | High | Uniform cathodic protection | Uniform cathodic protection |
| 5. | Initially low, then high | Low | High | Excessively overprotected | Slight corrosion during low current input; severe corrosion during high current input. |
| 6. | Initially low, then high | High | High | Sligh general corrosion during low current input, complete protection during high current input. | Slight general corrosion during low current input; complete protection during high current input. |
| 7. | Initially high, then low | Low | High | Complete protection possible with considerable overprotection also possible. | Severe corrosion possible. |
| 8. | Initially high, then low | High | High | Complete protection possible | Complete protection possible slight corrosion also possible |

* It is assumed that the cable sheath is in a duct system with minor soil or silt access and that it is fully immersed in duct solution.



Figure 16—Schematic illustration of specimen from gradient test with 40 ma and 12.5 pH.

6,000 ppm of CaCl₂ and 4,000 ppm NaCl in demineralized water and the current input to the cell was 40 ma. It represents an extreme of the service conditions of high salt concentration and excessive current density. The high current input caused the pH to go to a maximum value of 12.4 in this cell, and as a consequence a portion of the lead cathode strip above the water line developed the colored corrosion products which have become associated in the field with the so-called term "cathodic corrosion." This is not cathodic corrosion, however, but rather ordinary corrosion in an electrolyte which has been made highly alkaline by the large current. The cathodic protection system does not furnish adequate current to the meniscus region at and above the water line. Thus, the situation predicted by the Pourbaix diagram is obtained in which the lead surface is in equilibrium with PbO and $HPbO_2^-$ ions at pH values greater than about 9.5.

The appearance of and the type of the colored corrosion product on the lead cathode is not only a function of the pH but is dependent upon the potential as well. The appearance after three months operation of the lead cathode strip placed in this cell is shown schematically in Figure 16. It is seen that the colored corrosion products extend to a distance of 21 inches from the point of maximum current density. At the 21 inch distance the potential of the portion of the cathode below the water-line was about —0.60 volt ($H_2 = 0$) after the cell had been in operation for three months. It also must be noted that the formation of a colored corrosion film at and above the water line at this high-current cell does not appear to constitute a serious corrosion hazard under constant current conditions. The water-line corrosion film appears to be stable and does not thicken. It thus appears to be stable film representative of a passivation condition rather than progressive corrosion.

The most serious corrosion hazard at the water line was found in one gradient test with an input of 3 ma, which at this current level would attain a uniform pH of about 9.5 in a NaCl solution. The

cell solution was maintained, however, at a pH of 12.5 by the addition of NaOH. Under these conditions the low conductivity of the 100 ppm NaCl solution permitted a large portion of the 40 inch-long lead cathode to operate at a lower potential than required for full protection according to the Pourbaix diagram for this value of pH. In two months of operation the cathode developed a large number of pinholes at the water line which completely penetrated the sheet. The pinholes were found to be absent from the waterline area in the part of the cathode strip having the higher current density, for which the potential of the submerged part of the cathode was more negative than —0.53 volt ($H_2 = 0$). The rate of penetration by pinholing was so rapid that when translated into service life of actual cable sheath having a minimum of 0.150 inch wall thickness, it represented a life of less than five years.

From the results of the gradient tests it was possible to make some general observations on the probable behavior of lead sheathed cable in a cathodic protection system. These observations are given in Table 3 on the assumption that the sheath is fully immersed in duct solution. For conditions of partial immersion the water line attack could be expected to be many times more severe than as suggested in the table. The assumption of minor soil or silt contact as one condition upon which Table 3 was based is a consequence of the test conditions so far investigated. Tests are in prospect to determine the effects of soil contact with a lead cathode in a gradient system. The author's previous paper indicated that crusting of sheath due to soil contact could produce severe corrosion loss upon cessation of cathodic protection. The projected soil contact tests will indicate the effects of crusting during continuous cathodic protection.

*Effect of Low Salt Content and High pH*

Table 3 shows the greatest corrosion hazard to exist in a gradient system with low salt content and high pH produced either by local high current density or by intermittent, high current. It would appear from the table that high salt
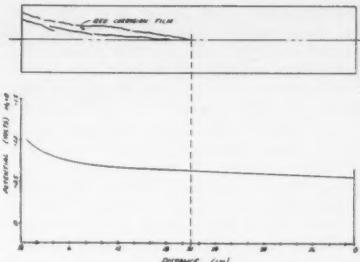
content of the sheath environment is an advantage. In the opinion of the authors it would be an advantage if cathodic protection in service could be based on constant and sufficient current, constant water level to give full immersion, and if no silt or soil were present to form crusts. In an excavation in Chicago to investigate condition of buried cable sheath, one cable was found to have a heavy accumulation of salt but was not corroded since the concentration of salt was able to maintain sufficient current to give complete protection.

The table shows that high salt concentration and high current do not constitute a corrosion hazard as long as these conditions are maintained. Even with sheath partially immersed in duct solution there is little corrosion hazard although a red-colored corrosion film forms above the water line. The red-colored film on a cathodically protected lead sheath is considered by the authors merely to be a "tell-tale" which indicates that the system is operating at a high pH. If the current to such a system were to decrease or cease altogether, failure due to corrosion would be most likely to occur in the regions having the colored film because of the high pH.

**Summary**

In has been shown that the pH established by the current input to a cathodically protected lead sheath is a major factor in determining the requirements for its protection.

It has been shown that the Pourbaix diagram is a reliable guide for determining the required potential for cathodic protection of lead sheathed cable under any pH which may be established in service.

It has been shown that the water line region of partially submerged lead cable sheath can be subject to severe and rapid failure in an environment of high pH while the sheath is theoretically under cathodic protection. At a pH of 12.5 it is necessary to establish a potential on the submerged portion of the sheath more negative than —0.53 volt ($H_2 = 0$) in order to obtain a service life on 0.150-inch thick lead sheath greater than five years. The Pourbaix diagram at 12.4 pH indicates a potential of about —0.62 volt ($H_2 = 0$) required for complete protection in the submerged portion of the cable. Thus more data are required to establish a more precise relationship between pH, protection potentials, and service life.

The concentration of salt in the environment of cathodically protected lead cable sheath may be an important factor in extending its service life. The distribution of cathodic protection current to the sheath is directly affected by the salt

concentration. The lower the salt content the greater the non-uniformity of current distribution and the greater the probability of failure at port.ons of the sheath remote from points in the system where current enters.

The above conclusion will no doubt startle many individuals who have had the responsibility of maintaining power and communication cable in heavily salted areas. High salt content has in the past been associated with so-called "cathodic corrosion" and early failure. The decreased resistivity of the earth due to salt content does cause greater amounts of current to exist in the cathodic protection system, but unless the high salt content is uniformly distributed in the immediate environment of the protected sheath, the current will be concentrated mainly at the points of entry. Since it has been shown in the

gradient tests that the high pH established by high current input is distributed throughout the system and that current distribution is a function of the salt content or conductivity, it will be seen that the distribution of salt in the entire cathodic protection system determines both the corrosion environment and the level of cathodic protection.

## Acknowledgements

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Chang Oh while holding a research assistantship in Electrical Engineering. The undergraduate laboratory assistants who contributed to the research effort are R. Oakes, W. Hanko, J. Gingerich.

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# Basic Concepts and Practical Aspects Of Field Corrosion Investigation*

By MAURICE A. RIORDAN

## Nature of Field Measurements

CORROSION OF metals in soil or water is an electro-chemical process. The corrosion or metal loss can be related to the direct current discharged from the metal surface at the metal/electrolyte junction. A scientific value known as the electro-chemical equivalent establishes the relationship between metal loss and current discharge. Therefore, a theoretical basis exists for calculation of metal loss from current, voltage and resistance measurements $(I = E/R)$.

Field corrosion investigations usually involve complex corrosion cells, heterogeneous environments and structures of relatively large physical dimensions. Innumerable anode-cathode combinations and configurations are possible. As a result, the circuit components involved in corrosion of many metallic surfaces are not readily definable and, most often, cannot be isolated. Therefore, any attempt to determine exact current densities and specific corrosion penetration rates would often involve measurements and techniques of a laboratory nature. In field investigations, practical limitations usually preclude such elaborate techniques.

The presence, absence, and relative severity of corrosion characteristics within a system can be determined by feasible field measurements. This information has practical application in corrosion control and is the usual objective of field investigations. This objective can be achieved by exploratory electrical measurements and interpretation of the resulting data. Both measurements and interpretation are based on knowledge of a simple corrosion cell and the measurable symptoms which such a cell exhibits.

Potential differences exist or develop on the surface (metal/electrolyte junction) of most structural metals when they are immersed in an electrolyte such as soil or water. These potential differences produce a battery action and current flow results. This action is illustrated schematically in Figure 1 (typical pipe line corrosion cell).

Corrosion takes place where the metallic ions are discharged from the metallic surface at the metal/electrolyte junction (anodic area). In conjunction with this action, ions from the electrolyte are accepted or transformed at adjacent or remote metallic surfaces that are less electronegative (cathodic area). The similarity between the corrosion process and battery action is apparent in Figures 1 and 2. Note that a metallic

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MAURICE A. RIORDAN, a partner in Rio Engineering Company, holds a degree in Metallurgical Engineering from Rensselaer Polytechnic Institute (1942) and is a registered professional engineer. Prior to his association with Rio Engineering Company he served in the U. S. Navy and then was engaged in electrochemical research and development work with Dow Chemical Company. He has been active in corrosion work and cathodic protection since 1946 and a member of NACE since 1948. Mr. Riordan is a member of several NACE Technical Committees and has served as an instructor at several NACE Corrosion Short Courses. He is currently serving as president of the Engineers Council of Houston.

circuit (base metal of pipe wall) and an electrolytic circuit exist. In the metallic circuit, the energy transfer involves electron flow. (In the corrosion cell, the base metal of the structure provides the metallic path.) In the electrolytic circuit, the energy transfer is accompanied by ion migration toward, and ion reactions at the metal surfaces.

From Figure 1, it can be deduced that DC potential gradients exist in the electrolytic and metallic circuit in conjunction with direct current flow. These electrical effects are related to the responsible anodes and cathodes. Thus exploratory measurements which reveal magnitude and polarity of potential gradients or current flow in

(1) The electrolytic circuit
(2) The metallic circuit
(3) Between the electrolytic and metallic circuit

can be interpreted in terms of corrosion.

## Measurement Techniques

Since field investigations are of an exploratory nature, the procedure to be employed varies with the specific conditions and objectives involved. The approach best suited to those conditions remains the prerogative of the Corrosion Engineer. Being a product of judgment, ingenuity and experience, field investigations are not rigid procedures. However, a general pattern

## Abstract

Electrical measurements are commonly employed to investigate the corrosion characteristics of structural metal systems in soil or water. Basic concepts applicable to field corrosion investigations of this type are presented.

The general nature of field measurements is discussed. Pertinent characteristics of a simple corrosion cell are reviewed. Practical aspects of typical field measurement techniques such as IR drop, surface potential, pipe to soil potential and resistivity are considered.

A Fundamental Corrosion Circuit Reference Diagram is presented for use in relating electrical field measurements to corrosion characteristics.

4.5.3

is discernible in the measurement techniques commonly employed. This pattern consists primarily of conventional electrical measurements which have been adapted to meet field requirements. Familiarity with conventional electrical measurement techniques is essential and is assumed throughout.

In conventional electrical measurement, circuit characteristics can be explored by metallic probes connected to a suitable measuring instrument. The same probe principle is employed in exploring the corrosion circuit. However, special probes are employed in the electrolytic portion of the circuit.

### IR Drop Measurements

From Figure 1, it is apparent that the direct current resulting from activity of the corrosion cell flows through the con-



Figure 1—Positive to negative potential gradient in a typical pipe line corrosion cell.



Figure 2—Basic battery circuit.
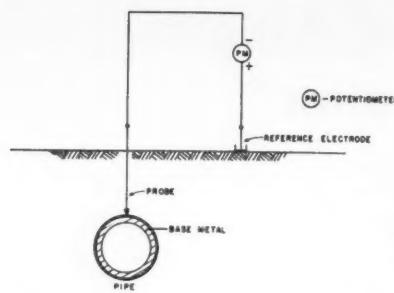
Figure 3—Typical pipe to soil potential measurement.



Figure 4—Hydraulic analogy—reference electrode.

tinuous metallic path available in the base metal of the structure. Therefore, the polarity and magnitude of potential measurements between the points in the continuous conductor will indicate the direction (polarity) and strength of current flow present (an IR relationship).

Metallic probes contacting the base metal of the conductor are employed in this measurement (see Figure 2, Probes 3 and 4). When metallic probes are used in this manner, it is the intent to investigate potential gradients within the metallic conductor. Junction potentials between the conductor surface and the electrolyte do not contribute directly to the potential difference measured.

Physical limitations involved usually preclude investigation of "local cells" in this manner. However, the IR drop measurement is often useful in evaluating direct currents of a long line nature or of appreciable magnitude as, for example, impressed currents of cathodic protection, stray currents, anodic and cathodic areas having appreciable separation, etc. (Where the resistance between probed points is known, the value of current can be calculated from $E = IR$). Thus, the metallic circuit alone can often be explored by IR drop measurements for symptoms characteristic of the corrosion process.

### Standard Half Cell

The use of a metallic probe in the electrolyte would often result in non-reproducible measurements due to the varying metal/electrolyte junction potential of the probe itself. Therefore, a probe of a more stable nature is required. A standard half cell is frequently employed. A standard half cell is an electrode-electrolyte combination that exhibits constant electrochemical characteristics and provides an essentially constant and reproducible potential. Copper sulfate, calomel and silver chloride electrodes are typical standard electrodes in field use.

The base metal of the standard half cell electrode also can be regarded as a metallic probe. The selected electrolyte of the half cell in which this metal probe is immersed results in a relatively constant metal/electrolyte potential of the half cell as a system. Thus, such a standard half cell is suitable for use as a probe in the electrolytic circuit.

### Two Electrode Measurements (Soil to Soil Potentials)

Theoretically, the potential difference between two standard half cells would be zero. Therefore, any potential difference obtained between two such standard electrodes (probes) positioned at two separate and distinct points in the electrolyte indicates the potential difference (polarity and magnitude) between the probed points of the electrolytic circuit itself. The potential gradient information provided by
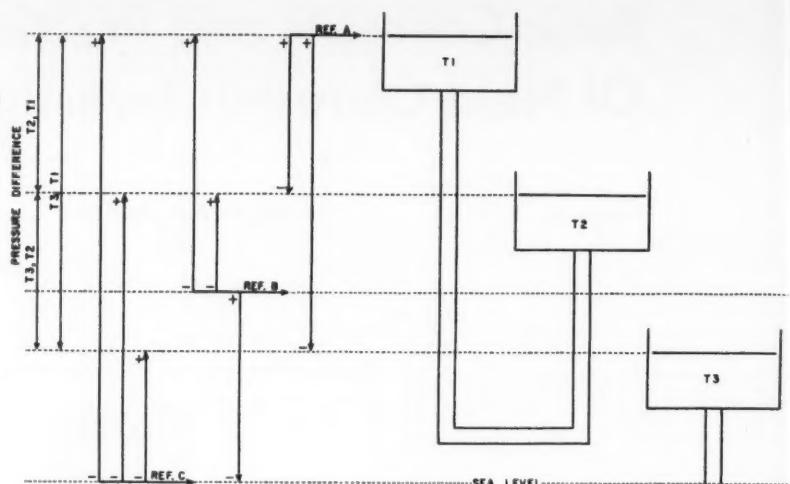
measurements of this type is valuable in indicating "hot spots" by soil to soil potential measurements (sometimes referred to as "surface potential" surveys), in investigating stray currents in the electrolyte, interference and other situations where a knowledge of the potential gradient in the electrolyte is useful. Again, magnitude and polarity have significance on the basis of Figures 1 and 2. The measurement is illustrated by Probes 1 and 2 of Figure 2. Basically, the two electrode measurement is also an electrolytic IR drop measurement. Thus, the two electrode method is useful in exploring the electrolytic circuit for corrosion symptoms.

### Structure to Electrolyte Potential (Pipe to Soil Potential)

When the potential difference between a point in the electrolyte and a point in the metallic circuit is to be investigated, the probes suitabe for use in each circuit are employed (i.e., standard half cell in electrolyte and metallic probe in metallic circuit). In general, the purpose of this measurement is to explore potential differences existing between the electrolyte and various points on the structure surface. Pipe to soil potentials are measurements of this type (Figure 3).

In the theory of the potential gradient measurements previously discussed, the magnitude of the reading was a direct measure of the potential gradient present. In the case of a structure to electrolyte potential measurement, however, the magnitude of the measurement is an indirect measure of the potential gradient of the system being investigated.

This can be emphasized if the probes in the measurement portrayed in Figure 3 are considered as being the base metal of the electrode and the base metal of the pipe. It is then obvious that two junction potentials are exerted between the probes (i.e., the metal/electrolyte junction potential of the standard electrode and the metal/electrolyte junction of the pipe). Other junction potentials, usually of minor significance, also exist.

The increment contributed by the standard half cell is constant by virtue of the constant junction potential it exhibits. Therefore, the standard electrode serves as a reference electrode in measurements of this type by providing a constant potential level to which other potentials are compared.

By hydraulic analogy, Figure 4 illustrates this reference principle and the variations resulting where different reference levels are employed. Typical reference levels employed in other energy system would be 110 volts to "ground," gas pressures compared to the "atmosphere."

The pressure at sea level, for example, could be considered analogous to the electrical pressure of a standard half cell used as a reference electrode. Thus, the algebraic differences between separate structure to reference electrode potential measurements reflected the potential difference between the portions of the circuit included in the respective measurements.

Previously, it was mentioned that the measurement objective here is to explore the variations in potentials at various points on the surface of the structure. Since these surface potential differences exist, current flow results inasmuch as the structure in its electrolyte provides a closed circuit for the battery action of the corrosion process. This current flow in turn, is identified with potential gradients in the electrolyte which influence the measurement between the probed points. Therefore, this reference electrode measurement also includes the net effect or resultant of IR drops as exerted between the probed points of the circuit.

Because of this closed circuit operation between anodes and cathodes on the surface of the structure, it is to be recognized that (1) the electrical position of the reference electrode is significant, (2) IR drop effects of closed circuit operation preclude the probability of true surface potential measurement of either anode or cathode without elaborate techniques. (Zero current flow in the measuring circuit is desirable in potential measurements using a reference electrode. Thus, IR drop effects resulting from the presence of the half cell reference electrode can be discounted.) By structure to electrolyte measurements, the potential difference between a point in the electrolyte and the base metal of the structure can be explored. These potential differences indicate the presence and relative severity of anodic and cathodic areas. This information can, in turn, be related to corrosion characteristics of the structure.
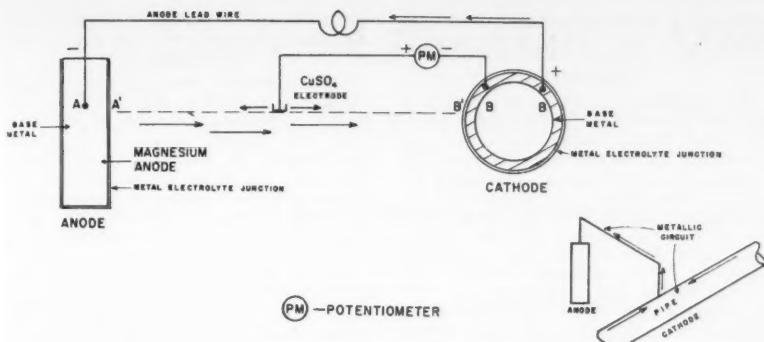
Figure 5—Anode-cathode system.



Figure 6—Typical potential gradients (corrosion cell).



Figure 7—Corrosion circuit diagram.

### Ammeter Measurements

Current measurements made directly through an ammeter and zero resistance current measurement follow conventional measuring techniques. In general, they are confined to metallic portions of the corrosion circuit available for insertion of a direct current measuring device. They indicate current strength and polarity. Basically, current measurement data of this type serve the same function as the DC current information indicated in IR drop measurements in the metallic circuit.

### Fundamental Corrosion Circuit Reference Diagram

Techniques for investigation of potential gradients and current flow have been discussed. A fundamental corrosion circuit reference diagram is offered in Figure 7 to indicate the relationship of measured DC potential gradients and current flow to the corrosion circuit. Figures 5 and 6 are used in the evolution of this diagram. Since the variations of I, R and E encountered in field corrosion cells are innumerable, Figure 7 can be regarded only as a schematic diagram which serves to illustrate the basic relationships involved. It is intended to be of practical rather than scientific value.

### Diagram Development

The development of the fundamental corrosion circuit reference diagram is discussed in detail since measurement techniques previously discussed are employed. To simplify development of this diagram a readily obvious anode-cathode system is utilized (i.e., a magnesium anode and pipe section). The pipe section is assumed to be a uniform potential surface and local cell action which exists thereon is temporarily ignored. The same assumption is also applied to the anode. This system is illustrated in Figure 5. "A" is a theoretical point in the base metal of the anode. A¹ is a theoretical point in the electrolyte of sufficient proximity to the point A that IR drop through the electrolyte between the base metal of the anode and "A" is negligible. B and B¹ are, respectively, similar points at the cathode. This identification of A, A¹, B and B¹ applies throughout Figures 5, 6 and 7. A metal/electrolyte junction exists between A and A¹ and between B and B¹. Thus, a potential difference exists between metal and electrolyte at this junction. The presence of the metal electrolyte junctions are represented schematically in Figure 5 by a line or film of exaggerated proportions around the anode and cathode.

It has been pointed out previously that the measured difference in potential between two balanced reference electrodes could be used to determine potential differences in the electrolytic circuit. By placing Electrode 1 at A¹ (Figure 6) and exploring the potential difference with respect to Electrode 2 as the latter electrode is moved progressively toward B,¹ a potential gradient resembling that of Curve I could result. Curve I is intended to indicate the trend of the potential gradient from anode to cathode in the electrolytic circuit. Thus, the specific shape of the curve employed has no exact significance.

Potential differences in the metallic circuit can be determined by placing Probe 3 at B and measuring the potential difference as Probe 4 is moved successively toward "A". A potential gradient resembling that of Curve II would result. Again, Curve II is intended only to indicate the trend of the potential gradient to the metallic circuit. (Some exaggeration of slope has been employed for diagram clarity.)

The relationship between Curve I and Curve II can be established by measuring the potential difference between the electrolytic circuit and the metallic circuit. Thus, a potential difference between a reference electrode at a known point on Curve I and the probe at a known point on Curve II will fix the potential relationship of the two curves. The resulting relationship is presented in Figure 7.

The potential difference from "A" to A¹ is composed predominantly of the metal/electrolyte junction potential of the anode and the reference electrode potential increment. Similarly, the potential difference from B to B¹ is composed predominantly of the metal/electrolyte junction potential of the cathode, the polarization potential increment (if any), and the reference electrode increment. (Polarization is the production of a new potential at the electrode surface by electro-chemical action. Polarization can take place at either the anode or cathode. Polarization at the anode has not been shown here.) The constant increment contributed by the potential of the reference electrode to all the potential differences measured is constant, as indicated in Figure 7.

In the electromotive series, the anodic or less noble metals are often represented as electronegative. Note that, at Point A, the prime metal of the magnesium anode is electronegative with respect to the adjacent electrolyte due to the potential developed at the metal/electrolyte junction. (The cathode is less electronegative.)

The net driving potential of the closed circuit can be approximated by the algebraic difference between A, A¹ and B, B.¹ This potential is distributed in the electrolytic and metallic circuits in proportion to their respective resistances and electro-motive forces. In the corrosion cell, the major portion of the circuit resistance usually exists in the electrolytic portion of the circuit.
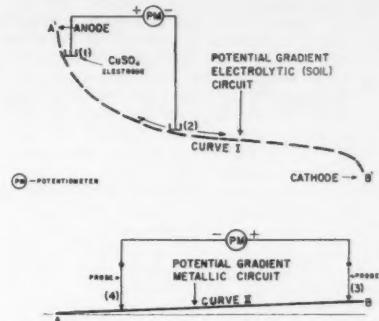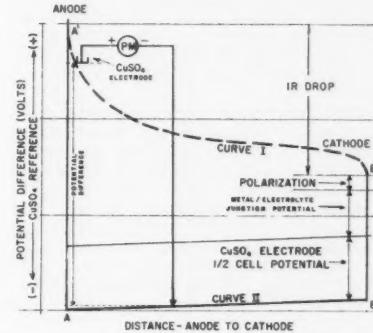
In the interest of simplicity, the anode and cathode have been assumed to be unipotential surfaces. This is not actually the case since, for example, the surfaces of the magnesium anode and the pipe section each exhibit individual anodic and cathodic properties. In turn, the general relationships exhibited in the diagram would exist between individual anodes and cathodes although the anode-cathode proximity might defy inspection by usual field techniques. This illustrates the relative nature of the terms anodic and cathodic and places emphasis on potential differences.

### Significance and Application

This fundamental corrosion circuit reference diagram is of a practical rather than scientific value. It illustrates the relationship and polarity of some measurable electric symptoms of the corrosion cell. Polarity relationships of metallic and electrolytic circuits are readily visualized. It offers a basis for relating potential gradient measurements to the corrosion circuit.

It emphasizes the presence of junction potentials, and shows the base metal of both anode and cathode as electronegative with respect to the electrolyte. It stresses the importance of potential differences. In reference electrode measurements (pipe to soil potentials), the magnitude is useful primarily in identifying potential differences present. It illustrates that the reference electrode functions as a probe.

The response of the reference electrode measurement to increased current result-

ing from application of cathodic protection is apparent in the following considerations. An increase in potential difference between a reference electrode position and the base metal of the cathode would result from (1) an increase in potential gradient of electrolyte at the cathode due to increased current flow toward the cathode, (2) polarization effects that may result from current flow. Thus, the base metal becomes more negative with respect to the electrolyte. As a result, the magnitude of pipe to soil potentials tends to increase when cathodic protection is applied. (This also emphasizes the relative nature of anodes and cathodes.)

By inspection, the practical significance of the electrical position of the reference electrode with respect to anode and cathode is apparent. The reference electrode measurement usually indicates a value less than the anode potential and greater than the cathode potential as determined by the reference electrode position with respect to the potential gradient in the electrolyte.

The diagram recognizes the application of Kirchhoff's Law to any *instantaneous* condition as the algebraic sum of electromotive forces and voltage drops around the closed circuit is zero. (Caution is advisable in the application of this law inasmuch as electro-chemical changes with time can occur within the cell.) Although the closed circuits of heterogeneous corrosion cells are difficult to identify, recognition of the implications of this law can be helpful in pursuing corrosion investigations.

## Resistivity

The potential differences discussed above provide information on the driving forces within the corrosion cell. In calculating the strength of current flow responsible for corrosion, resistance to current flow should be considered in conjunction with the driving force $(I = E/R)$. Resistance can be calculated from $R = \rho \, L/A$. ($\rho$ = specific resistivity, L = conductor length, A = cross-sectional area.) Because of the heterogeneous nature of corrosion cells, L and A are not readily definable. However, the specific resistivity of the electrolyte can be reasonably indicated by various field measurement techniques (four pin method, soil box, etc.). As a direct multiplier in the $R = \rho \, L/A$ equation, the specific resistivity of the electrolyte is a relative indication of circuit resistance and electro-chemical corrosivity of the environment since the major portion of the total circuit resistance is usually in the electrolyte.

Again, from $R = \rho \, L/A$, it is apparent that the circuit resistance is also a function of the length of the electro-chemical path between anodes and cathodes and the cross-sectional area of these paths. Thus, anode and cathode areas and the effective electrolytic paths between them are entitled to consideration wherever possible, in a further evaluation of the corrosion interpretations based on resistance.

## Conclusions

Field corrosion investigations by electrical measurement depend upon exploration and identification of electrical symptoms characteristic of the corrosion process. DC potential gradient, current and resistivity characteristics are typical of these symptoms. Conventional electrical measurement techniques have been adapted to field measurement of these characteristics.

The potential gradient, current and resistance relationships of a simple corrosion cell provide a basis for interpretation of these field measurements. By proper interpretation, the presence, absence and relative severity of corrosion is indicated. Thus, practical information can be obtained in the field by practical means.

The fundamental corrosion circuit reference diagram has value in relating field measurements to the corrosion characteristics of the structure under investigation.

The procedures and criteria to be employed in field corrosion investigations vary with the technical and practical aspects involved. Obviously, the application of knowledge, experience and judgment is required in proceeding from the basic principles and techniques to the optimum procedures and criteria applicable to specific corrosion investigations.

**Any discussions of this article not published above
will appear in the June, 1958 issue**

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# An Electrical Resistance Method of Corrosion Monitoring In Refinery Equipment*

### By A. J. FREEDMAN, E. S. TROSCINSKI and A. DRAVNIEKS

## Introduction

WITH CORROSION costs to the oil refining industry approaching $300,000,000 annually, the detection, measurement, and elimination of corrosion in process units is becoming an increasingly urgent problem. The development of new refining processes involving extreme temperatures and pressures with corrosive fluids has created new and previously unknown difficulties requiring careful observation and control of corrosion rates. The effects of process variables, construction materials, corrosion inhibitors, and protective coatings on corrosion must be evaluated under actual operating conditions. Solutions to new and unexpected corrosion problems must be found as quickly as possible. Sensitive locations in new units, where corrosion might be expected, must be monitored frequently. Safety checks must be maintained at points of high corrosion throughout the refinery.

## Conventional Corrosion Monitoring Methods

Until recently, only three general methods were available for corrosion investigations in refinery process equipment. These include unit inspections, use of corrosion coupons and analyses of effluent streams for metal content.

In modern complex refineries, the limitations and disadvantages of these procedures are becoming increasingly apparent. For example, unit inspections are a necessary part of refinery maintenance programs. They provide valuable information concerning long term corrosion rates. However, inspection data will not detect rapid fluctuations in corrosion rates and are not useful for fast quantitative evaluation of protective measures.

Analyses of tail waters and effluent streams for metal content must be interpreted with great caution. Data averaged over long periods of time may be related significantly to general corrosion rates in some cases. However, fluctuations in the composition and detergent action of product streams can have tremendous influence on the distribution of corrosion products formed within the unit. For example, a sudden increase in iron content of a condenser tail water may result from a loss in inhibitor effectiveness, an increase in detergent action, a decrease in pH, an increase in the percent of water in the effluent stream, a change in the composition of the stream, or any combination of these and other variables. In addition, since corrosion products generally can be formed throughout a unit, the determination of corrosion rates at a particular location is especially difficult by this method.

Coupon studies represent the best of
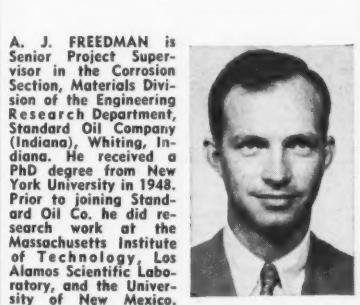
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the classical methods for refinery corrosion investigations. Coupons of any material can be inserted at specific locations, and will measure quantitatively the average corrosion rate over the period of exposure. In some cases, retractable holders can be used to remove coupons while a unit is "on stream." Generally, however, coupons can be inspected only during shutdowns. For this reason, sudden changes in corrosion rate caused by short-range changes in process variables are difficult to detect with coupons.

## The Electrical Resistance Corrosion Probe

What are the requirements for a good refinery corrosion-monitoring device?

## Abstract

A corrosion test system based on the electrical resistance method permits continuous monitoring of corrosion rates in refinery equipment without interrupting normal operations. Corrosion decreases the cross-section, and consequently the electrical conductivity, of a metal specimen exposed to refinery fluids at high temperatures and inaccessible locations. From the decrease in conductivity, or increase in resistance, the amount of corrosion which occurs between measurements can be determined. The system has been used successfully under all conditions of temperature and pressure encountered in a refinery. It has measured corrosion rates in vapor and liquid phases, with both oil and aqueous media.

With the aid of the corrosion probe, corrosion rates in operating refinery equipment have been determined quantitatively in a few hours' time, as compared with months required for coupon measurements, water analyses, and unit inspections. Refinery corrosion inhibitors have been compared rapidly in actual use. Effects of changes in unit operating procedures upon corrosion rates have been observed shortly after the changes were made. Sensitive locations where corrosion is expected have been monitored frequently.          2.2.1

First, the method must be capable of detecting corrosion in operating equipment, so that protective measures and process variables can be evaluated under actual operating conditions. Second, the method must be rapid, so that solutions to urgent problems can be tested without delay, and so that lengthy, expensive experimental programs can be avoided. Third, the method must be accurate and reproducible, to ensure that data obtained with this method will correspond to actual corrosion rates at the point of measurement. Fourth, the method must be sensitive, so that low corrosion rates can be measured in reasonable times, and so that small changes can be detected. And perhaps most important, the measurements must not interfere in any way with normal refinery operations.

A corrosion-monitoring procedure which fulfills all of these stringent requirements is the conductometric, or electrical resistance method. This method has been used extensively for industrial laboratory corrosion testing and in plant operations. A large number of electrical resistance corrosion probes have been installed in refineries for many different applications.

The electrical resistance method of measuring corrosion has been discussed in papers from this laboratory published during 1954 and 1957,[1,2] and by other authors.[3,4] Briefly, the method consists of measuring the change in electrical resistance of a metal specimen placed in a corrosive medium. Since the resistance of an electrical conductor is inversely proportional to its cross-section, the change in resistance of the specimen with time can be related to the amount of corrosion that occurs during the experiment. A number of different electrical circuits may be used for measuring the
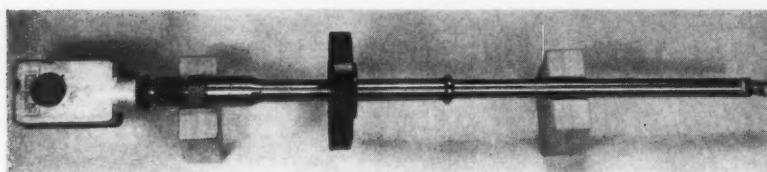
Figure 1—Refinery corrosion probe.
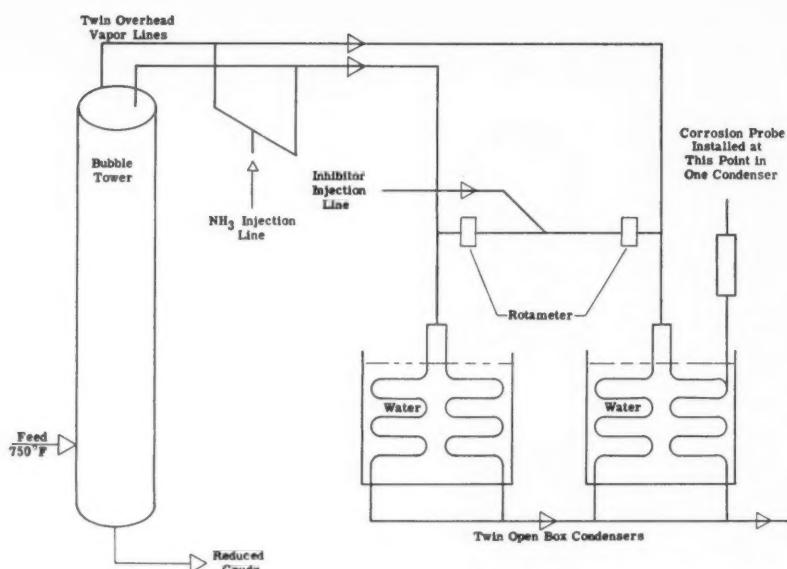


Figure 2—Pipe still flow diagram.

resistance changes. Some of these instruments now are available commercially.[5, 6]

Figure 1 is a photograph of a typical refinery corrosion probe. This probe is designed to fit into a conventional one inch open-end thermocouple nozzle with ball-and-socket joint and flanged connections. The probe is ruggedly constructed and designed to be completely reliable under all conditions of temperature and pressure normally encountered in the refining industry.

The electrical resistance measurements are not influenced by accumulated corrosion products. With coupons, however, the necessity of removing the corrosion products before each weight loss determination limits the sensitivity of the experiments. For example, simple calculations show that at a corrosion rate of .01 inch per year, a retractable coupon 0.5 inch by 3 inches will lose 10 mg per day. Under these same conditions, the resistance of a typical probe specimen will increase from 0.2 percent to 1.0 percent per day, depending upon the initial thickness of the specimen. However, over a one-day exposure at this corrosion rate, only very small amounts of corrosion products will accumulate on the coupon. For this reason, the errors introduced in cleaning the coupon will be large and variable, and in some cases may overshadow completely the 10 mg absolute weight loss. Much longer time intervals would be required to provide satisfactory accuracy in this weight loss determination.

On the other hand, the accuracy of the

resistance determination is influenced only by the measuring instrument used and by any undetected changes in probe temperature during the brief period required to read the meter. Errors of 1 percent in this measurement are unusual. In addition to this advantage of the corrosion probe over retractable coupons, the convenience of measurement should be considered. Corrosion probe data can be obtained in a few minutes time each day. Coupons, however, must be retracted and replaced, sometimes in difficult or dangerous locations. Then the used coupons must be transported to the laboratory for laborious cleaning and weighing operations. Thus, the corrosion probe provides much greater sensitivity, accuracy, and convenience than coupons for frequent measurement of corrosion rates.

It is important to remember that data determined with the corrosion probe represent corrosion rates on the probe specimen at the point of insertion. These rates do not necessarily correspond exactly to general corrosion rates in an operating unit. Corrosion coupon data also must be interpreted in this way. This is not a serious difficulty since in most cases only comparative corrosion rates are of interest. However, since the probe specimen generally is placed close to the vessel wall and is made from the same material as the vessel unless other metals are being examined, probe results and actual plant corrosion rates have shown very good agreement. For this reason, and in order to make the data readily understandable to refinery oper-

ating personnel familiar with coupon experiments, the corrosion probe results have been expressed in terms of inches per year penetration rather than in arbitrary electrical units.

## Evaluation of Corrosion Inhibitors

One of the most important applications of the electrical resistance corrosion probe is in the field evaluation of alternative corrosion-protection measures. For example, the probe has been used to evaluate a series of commercially-available corrosion inhibitors for use in a pipe still light naphtha condenser.

Figure 2 is a schematic diagram of the overhead condenser system on this pipe still. Twin overhead lines pass through parallel open-box type condensers. Ammonia for pH control is injected into each line near the top of the tower, and inhibitor is injected through rotameters mounted just ahead of each condenser. The corrosion probe was installed in the first return bend of one of the condensers. Temperatures at this point in the condenser ranged between 195 F and 215 F at a pressure of 1-5 psig. Conditions are thought to be typical of aqueous condensate type corrosion in the presence of corrosive oil phases. Previous experience indicated that in the absence of inhibitors, this first return bend was subject to severe corrosion. During these experiments, the pH of the overhead tail water was maintained close to 8, and iron analyses were made at frequent intervals.

Figure 3 presents the results of the corrosion probe measurements. In this graph, the total amount of corrosion measured on the probe is plotted on the vertical axis, against time on the horizontal axis. Thus the curve starts at zero corrosion and proceeds to higher values. The slopes of the lines represent corrosion *rates*. Horizontal lines indicate no corrosion with time, while nearly vertical lines represent high corrosion rates.

Three different inhibitors were tested. In addition, a short initial measurement was made with no inhibitor, as shown at the start of the curve.

Two different types of crude were fed to the unit during the experiment, as shown by the dotted and solid portions of the curves. Apparently the changes in feed had no significant effects upon the measured corrosion rates.

The differences in effectiveness of these three inhibitors is strikingly apparent from this graph. The corrosion rate dropped from .25 inch per year with no inhibitor to .02 inch per year with inhibitor 1 at 11 parts per million. When the dosage was increased to 22 parts per million the corrosion rate decreased to .01 inch per year. Then immediately after the inhibitor was changed to compound No. 2, the corrosion rate dropped to zero. When the dosage of compound 2 was reduced from 20 to 10 parts per million, the corrosion rate increased only to a barely measurable value, .001 inch per year. However, when compound 3 was introduced, at 30 ppm, the rate immediately increased to .08 inch per year.

Because of operational problems, the unit was shut down briefly two times during this test. Conceivably, if corrosion coupons had been used for the investigation, the coupons could have been inspected during these shutdowns, and also at the end of the test. It is apparent, however, that the detailed quantitative comparison of corrosion rates with inhibitor concentrations shown here could have been obtained only with difficulty
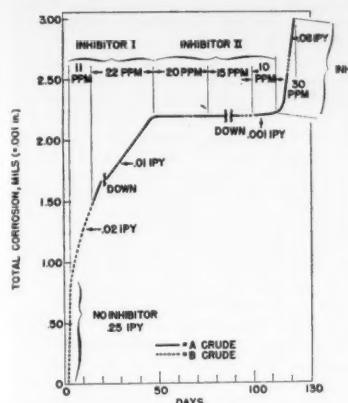
Figure 3—Corrosion probe measurements (light naphtha condenser).



Figure 4—Total iron content of overhead stream (light naphtha condenser).



Figure 5—Corrosion probe measurements in pressure still.



Figure 6—Corrosion probe measurements in oil-treating unit.

by means of coupons. Perhaps most important, coupon data would not have illustrated the striking changes in corrosion rate that can occur when one inhibitor is substituted for another during normal operations.

Figure 4 shows the iron concentrations in the aqueous phase from the light naphtha condenser which were obtained during the period of this investigation. The random nature of these data is apparent from the graph. Note also that although the corrosion rate as measured with the probe dropped to zero immediately after inhibitor 2 was added, the iron analyses remained high for about two weeks. This is a good example of the effects that detergent action can have on the metal content of a refinery stream. Even after low iron counts and clear water were obtained, the data show so much variation that effects of changes in inhibitor concentration are completely submerged. Certainly the quantitative comparison of inhibitors made on the basis of the corrosion probe cannot be deduced from the iron analyses.

### Evaluation of Process Variables

Another important application of the corrosion probe has been to evaluate the effects of process changes upon corrosion rates. In a group of pressure stills, considerable difficulty was experienced with both corrosion and coking. In an effort to determine the best operating conditions from a corrosion standpoint, corrosion probes were placed in a number of towers in this group of stills. These towers operate at about 850 F and 300 psig. Figure 5 presents data obtained with one of these probes.

During the first four days of this experiment, the corrosion rate rose steadily as indicated by the increasing slope of the curve. Progressive changes in unit operations were made at times marked by the arrows. After the first change, the slope of the corrosion curve decreased to zero. The second change caused an immediate increase in corrosion rate, but control was re-established quickly and the rate returned to zero. After the third progressive change in operating conditions, the corrosion rate gradually increased until the end of the experiment. The final slope of the curve corresponds to about .44 inch per year corrosion.

In order to conduct these experiments, it was necessary to measure corrosion rates in high temperature, high pressure
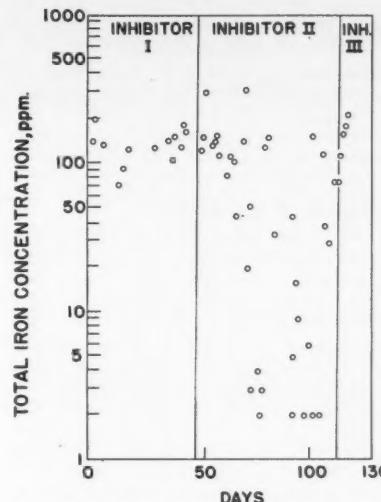
units during normal operations. Any down time required to change coupons or make caliper readings between operational changes would have introduced additional variables and obscured the results of this test. In addition, only average corrosion rates between shutdowns could have been obtained. With the electrical resistance corrosion probe, it was possible to observe the effects of changes in operating variables upon corrosion rates almost immediately after the changes were made, and to follow closely the variations in corrosion rate with time.

Figure 6 presents another example of the use of the corrosion probe to observe the effects of operational changes upon corrosion rates. These data were obtained in a lubricating oil treating plant. This unit handles many different types of feed stock, with each stock being treated on an individual basis to produce a uniform quality product. Several different degrees of acid and caustic washing are employed, together with other purification steps, all on feed stocks of varying composition. On this graph, the arrows indicate dates on which the feed stock was changed and time intervals during which acid treatments were used as part of the process.

The data show that except for a period of about ten days when no corrosion occurred, the corrosion rate during this test varied continuously between about .01 and .04 inch per year. There is no apparent correlation between feed stocks or acid treatments and corrosion rates. These results were unexpected, since it had been assumed that corrosion in this unit occurred primarily during periods of acid treatment. Since feed stocks were changed every 3 to 5 days during this experiment, the absolute amounts of corrosion that occurred during each interval were very small.

Without the corrosion probe, it would have been impossible to determine whether or not individual feed changes had appreciable effects on the corrosion rate. A few iron analyses were obtained on effluent water from this unit. However, because the composition of the feed and other process variables changed so frequently during the experiment, the data fluctuated widely and showed no valid correlation with the corrosion probe results.
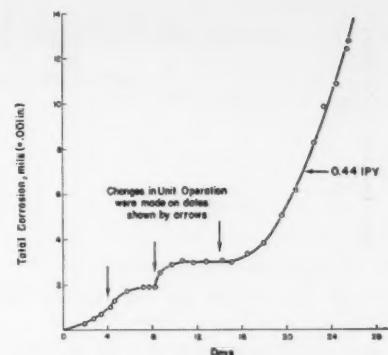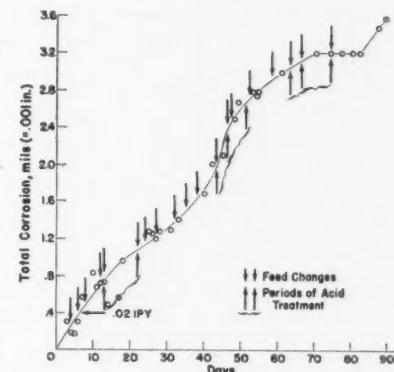
### Corrosion Monitoring with Probes

The development of new octane-improving operations and petrochemical processes in recent years has created many new and unusual corrosion problems. In many cases, it has been difficult to predict, on the basis of laboratory and pilot plant studies, what types of corrosion to expect. Plant experience with these new processes has not been sufficient to expose all of the corrosion problems which may exist. Therefore, it is important to monitor frequently the sensitive locations in these units. For example, when Whiting No. 1 Ultraformer went on stream in 1956, five corrosion probes were installed at points where corrosion had been experienced in other units. All of the probe measurements were obtained with one control circuit in a central location. Figure 7 shows some typical data obtained with two of these probes.

For clarity, the zero corrosion line in both of these graphs is raised above the horizontal axis. At location A, no measurable corrosion occurred during the first fifty days of the monitoring period. After that time, a small amount of corrosion was detected. However, the corrosion rate, .006 inch per year, is completely negligible in this case. At location B, no measurable corrosion was observed during the entire monitoring period. Thus, corrosion probes have provided concrete evidence that sensitive locations in a new and expensive refinery unit are in no danger from corrosion at present.
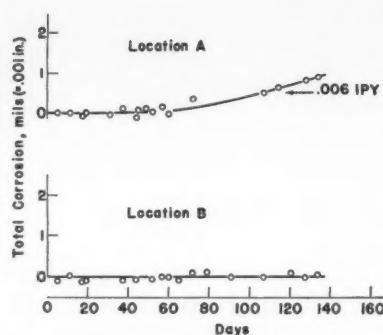
Figure 7—Whiting Ultraformer corrosion probe data.

## Conclusion

The electrical resistance corrosion probe provides quantitative measurements of corrosion rates in refinery equipment without interfering in any way with normal operations. With this tool, the corrosion engineer can evaluate rapidly and accurately a series of corrosion-protection measures. He can observe the effects of operational changes shortly after the changes are made. He can monitor frequently, sensitive locations in new units where corrosion might be expected. As refining and petrochemical processes become more and more complex, the electrical resistance corrosion probe should become an increasingly important instrument for corrosion investigations of all types.

### References

1. A. Dravnieks and H. A. Cataldi. *Corrosion*, 10, 224 (1954).

2. A. J. Freedman, A. Dravnieks, W. B. Hirschmann, and R. S. Cheney. *Corrosion*, 13, 89t (1957).

3. G. A. Marsh and E. Schaschl. *Oil and Gas Journal*, 54, No. 29, 135 (1955).

4. G. A. Marsh and A. V. Koebley, Jr. *Oil and Gas Journal*, 54, No. 29, 139 (1955).

5. A. Dravnieks, U. S. Patent No. 2,735,754, and other applications pending.

6. D. H. Stormont. *Oil and Gas Journal*, 55, No. 3, 85 (1957).

## DISCUSSION

### Question by Richard E. Baus, Gulf Oil Corporation, Philadelphia, Pennsylvania.

Do you find it necessary to vacuum-anneal probes and will this improve reproducibility to a significant extent?

### Reply by A. J. Freedman:

We never have found it necessary to apply any special surface preparation to corrosion probe specimens for refinery use. Because these specimens are much thicker than those employed in laboratory work, and because the experiments are carried out over long periods of time, corrosion in the surface layer of the specimen constitutes only a small fraction of the total corrosion measured with the probe. In laboratory work, however, where very thin specimens are employed and a high degree of sensitivity is required for short-term testing, vacuum-annealing has been adopted as standard procedure for preparing reproducible metal surfaces.

### Question by Donald L. Burns, Gulf Oil Corporation, Port Arthur, Texas:

Was the instrument and probe used of Standard Oil Company or of commercial origin?

### Reply by A. J. Freedman:

The corrosion probes and measuring circuits used in this work were designed and manufactured by the Standard Oil Company (Indiana). Instruments and probes manufactured by the Crest Instrument Company, Santa Fe Springs, California, combine the developments of both Standard Oil Company (Indiana) and Crest Instrument Company, and embody the principles of Standard's U. S. Patent 2,735,754 under which Crest is licensed.

### Discussion by F. L. LaQue, The International Nickel Company, Inc., New York, New York:

In view of the fact that there is no opportunity to observe the nature, form and distribution pattern of the corrosion that is being measured by the probe, it is suggested that the results be expressed simply in terms of change in resistance as a function of time rather than as an indicated rate of penetration of corrosion with time. The conclusions that can properly be drawn and the action that may be taken based on them on the basis of the direct expression of what is being observed should be as usable as by reference to some calculated rate of corrosion. At the same time, one would avoid difficulties that might result from misuse of the implications of the corrosion rate figures by readers of the report who are less aware of the limitations of such data than are the original investigators.

It seems also in order to draw attention to certain limitations of test specimens of this sort. They do not permit observations of hot or cold wall effects, nor peculiar effects of velocity or turbulence that may be encountered by the corrosion probes to a much different extent than other surfaces that may be in contact with the same corrosive environment where peculiar turbulence may exist. These limitations are, of course, not peculiar to the corrosion probe test specimens, but should be kept in mind.

### Reply by A. J. Freedman:

Mr. LaQue's comments are certainly correct. However, we have used well-known corrosion penetration units in order to make the data readily understandable to refinery personnel and others accustomed to common types of corrosion measurements. The determination of corrosion by both weight loss techniques and the electrical resistance method is limited to uniform corrosion over the entire specimen surface. In either case, pitting and other forms of localized attack can be detected only by additional measurements on the specimen, usually visual in nature.

**Any discussions of this article not published above will appear in the June, 1958 issue**

# High Temperature Oxidation
## Of Iron-Nickel Alloys*

By M. J. BRABERS and C. E. BIRCHENALL

## Introduction

THIS PAPER represents an extension and refinement of experimental research on the subject of high temperature oxidation of iron-nickel alloys reported earlier.[1] It had been established that iron alloys of low nickel content oxidized to produce a layer of wüstite free from dissolved nickel,[2] overlaid with layers of nickel-free magnetite and hematite.[1] The nickel was enriched in the metal layer near the external scale. The subscale which formed in this region was initially wüstite but later became a spinel as the nickel content in the alloy rose. In cases where the supply of oxygen was cut off and the specimen equilibrated by continued heating, the oxide was entirely converted to wüstite in the time allowed except for small amounts of spinel found as liners of cavities in the subscale region. When the initial nickel content of the alloy was sufficiently high, wüstite was not one of the products at any stage of the reaction.[3] The general structure of the Fe-Ni-O phase diagram as it relates to the iron-rich alloys, wüstite and the spinel oxide, was deduced from the observations.

These conclusions which involved some assumptions about the residual displacement of the system from equilibrium have been substantiated by experiments more carefully controlled to yield better equilibration. Additional observations have been made. A more detailed mechanism for the oxidation of iron-nickel alloys and for the homogenization of the resulting composite is proposed. A part of the ternary phase diagram is given at 1050 C.

## Experimental Procedure

In the earlier work a fairly thick oxide was applied by oxidation of an iron-nickel alloy in air or oxygen for times of about three days. Then the system was flushed with argon, sealed off under the inert atmosphere, and equilibrated for a week to ten days. In this new work the oxidation was carried out in very brief stages with partial equilibration periods between oxidizing stages. The total thickness of oxide formed was usually less, resulting in a smaller departure of the alloy composition from the starting value. The final equilibration period was extended greatly. The total time was more than 1000 hours.

(1) Wüstite is an oxide with the NaCl structure, with iron and oxide ions on alternate sites. A high concentration of vacancies in the iron sites prevents the stoichiometric composition FeO being attained in an equilibrium phase. Magnetite is a spinel crystal of composition close to Fe₃O₄. Hematite is a rhombohedral crystal of composition Fe₂O₃.

**Brabers**      **Birchenall**

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C. E. BIRCHENALL has served as associate professor of chemistry, Princeton University, since 1952. He holds an AB from Temple University, and MA and PhD from Princeton. From 1946 to 1952 he was a member of the staff of the Metals Research Laboratory at Carnegie Institute of Technology and during 1951-52 was assistant professor of metallurgical engineering, before leaving for Princeton. His research interests include: Diffusion of solids, oxidation of metals and alloys, thermodynamics and alloy systems. He has published numerous papers on these subjects.

These modifications serve to suppress large concentration changes in the alloy phase just below the oxide layer which may give rise to the temporary formation of phases not to be expected in the equilibrium mixture.

As before, the equilibrated specimen was quenched in air. During cooling an external layer of magnetite formed which often was fairly thick compared with the external scale produced at temperature. However, because of differences in geometry and composition, there was no difficulty in distinguishing this material from any other spinel product in the sample.

In other respects the procedure was essentially the same as that used before.[1]

## Results

### Metallography

The less vigorous oxidizing conditions and longer equilibration resulted in substantial changes in microstructures. The 15 percent[2] Ni alloy had previously shown copious porosity lined with spinel even though most of the surrounding subscale oxide was wüstite. In this in-

(2) All compositions are in weight percent except on the phase diagram (Figure 3).

## Abstract

Iron-nickel alloys of several compositions were oxidized in oxygen at 1050 C. Subscale formed preferentially at grain boundaries. Equilibration under an inert atmosphere occurred mainly by the dissolution and diffusion of oxygen in the alloy phase. Porosity developed in the subscale region during equilibration, then began to sinter out on longer heating.

Several features of the iron-rich corner of the ternary phase diagram were determined. The three phase triangle was shown to have apices near 55 weight percent Ni in the alloy phase, 52.6 atomic percent oxygen in the wüstite phase, and 10 weight percent Ni in the spinel phase. Ni is virtually absent from the wüstite phase. Consequently the wüstite in equilibrium with an iron-nickel alloy has a higher oxygen content (lower iron activity) than when in equilibrium with pure iron at the same temperature.

The reduction in the concentration difference between the extremes of the wüstite layer on an iron-nickel alloy as compared with one on pure iron (with an overlying layer of magnetite in each case) leads to a lower growth rate of the wüstite phase on the alloy. By reference to the relative rates of growth on pure iron, it is anticipated that the elimination of wüstite as a stable phase should lead to a decrease in the overall oxidation rate by a factor of about 20, the actual rate determined by the growth of the spinel phase.     3.2.3

stance there was much less porosity, although some still remained. The spinel was entirely absent. A microstructure, typical except for an unusual amount of porosity, is shown in Figure 1.

During the very long equilibration period, the subscale was observed to pervade the whole cross section of the sample, presumably by the dissolution of some of the external scale followed by diffusion of oxygen into the alloy where new oxide can precipitate. The preference for subscale formation at grain boundaries, shown in Figure 2, may be the result either of more rapid oxygen diffusion along the boundaries or of easier nucleation of the precipitate at the boundaries. In any case, it is evident that equilibration does not have to wait for the very slow Fe-Ni diffusion process.

The morphology of the subscale shows some interesting features, other than its grain boundary preference. A particularly suggestive arrangement is the "half moon effect" seen in Figure 3 where the end of one of the arms of a wüstite particle is separated from the main body by the intrusion of metal. It is suspected that in specimens homogenized for briefer periods this would have been a spinel-lined cavity formed by reduction of subscale spinel as the wüstite subscale penetrated to greater depths in the specimen. Wüstite replaces the spinel in the subscale when the nickel-rich alloy layer just below the scale is impoverished by diffusion during the equilibration cycle. The porosity may have been eliminated later by sintering of the alloy.
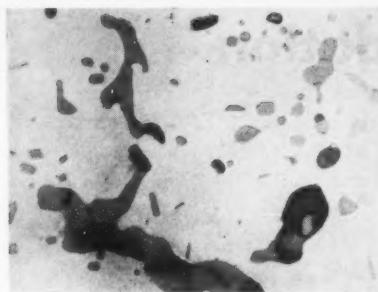
Figure 1—Subscale microstructure for 15.06 weight percent nickel alloy oxidized intermittently in air for 214 hours and then annealed in inert atmosphere for 1003 hours. Cavities were selected in order to show the absence of spinel. Original magnification, 500X, actual magnification after reduction for engraving purposes, 250X.



Figure 3—Mixed wustite and spinel subscale in same specimen as shown in Figure 2. The wustite shows a mottled surface on etching in dilute HCl; magnetite remains smooth. Original magnification, 1350X; actual magnification after reduction for engraving purposes, 775X.



Figure 4—External scale on specimen in Figure 2 showing (a) magnetite layer formed by oxidation on cooling, (b) magnetite formed by precipitation from wustite on cooling, (c) spinel in contact with wustite and alloy at temperature, (d) wustite and (e) mounting plastic filling cavity. Original magnification, 1350X; actual magnification after reduction for engraving purposes, 625X.
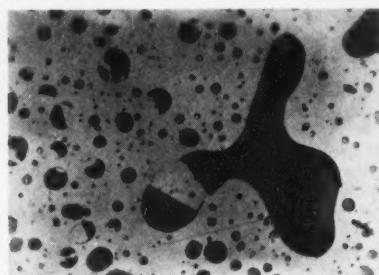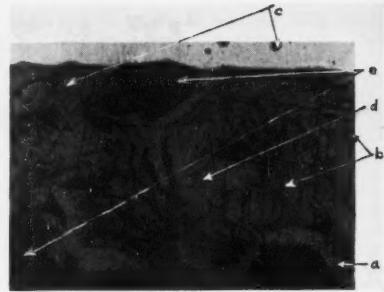


Figure 2—Subscale microstructure in 48.5 weight percent nickel alloy oxidized and homogenized intermittently for 1102 hours. This photograph shows the precipitation of mixed wustite and spinel deep within the specimen with larger particles outlining the grain boundaries. Original magnification 200X; actual magnification after reduction for engraving purposes, 100X.

### TABLE 1—Summary of Lattice Constant Determination

| Run | External Scale | | Subscale | | |
| --- | --- | --- | --- | --- | --- |
| | Wustite | Spinel | Metal (f.c.c.) | Wustite | Spinel |
| 17 | $4.28_0$ | $8.38_7$ | $3.58_0$ | $4.28_5$ | $8.35_8$ |
| | $4.28_5$ | $8.36_8$ | $3.58_6$ | $4.28_5$ | $8.37_2$ |
| | | | $3.58_8$ | $4.28_5$ | $8.37_2$ |
| 18 | $4.28_5$ | $8.39_3$ | $3.57_3$ | $4.28_9$ | $8.37_6$ |
| | $4.28_5$ | $8.39_6$ | $3.57_0$ | $4.28_3$ | $8.37_6$ |
| | $4.28_2$ | $8.38_0$ | $3.56_0$ | $4.28_0$ | $8.36_5$ |
| | | | $3.57_4$ | $4.28_0$ | $8.35_7$ |
| | | | $-3.56_2$ | $4.28_2$ | $8.36_4$ |
| | | | $3.56_2$ | $4.28_3$ | $(8.38_7)$ |
| | | | $3.57_0$ | $4.28_5$ | $(8.40_8)$ |
| | | | $3.56_8$ | $4.28_3$ | $8.37_5$ |
| 19 | None | $8.41_7$ | $3.53_0$ | None | $8.38_1$ |
| | | $8.40_7$ | $3.54_0$ | | $8.38_6$ |
| | | $8.38_9$ | $3.53_5$ | | $(8.36_8)$ |
| | | $(8.37_6)$ | $3.54_1$ | | $8.38_9$ |
| | | | $3.53_7$ | | $8.38_8$ |

Note: The lattice constants are given in A°. The successive values are for different layers as the surface was ground away. Values in parentheses are uncertain because of the low intensities of the diffraction lines employed.

Coexistence of three phases in mutual contact has been found, particularly in the subscale regions, indicating that the specimen composition lies in the three phase triangle. Figure 4 shows such a microstructure for an alloy originally containing 48.50 percent Ni. The spinel in this case is not associated with cavities and is not the result of incomplete equilibrium. The spinels in such aggregates which existed at the equilibration temperature, photograph darker than the wustites, presumably because of the nickel content of the spinel. On the other hand, the spinels formed by external oxidation during cooling in air or by precipitation from wustite are lighter than the wustite, since they contain no nickel. Thus it is very easy to distinguish the spinel which was at the equilibrium temperature from that formed on cooling.

It has been noted that for increased nickel content of the alloy, the amount of magnetite precipitated in the wustite during cooling also increased. Thus, in agreement with the observations of Kubaschewski and vonGoldbeck[4] and Oriani,[5] it was found that the wustite became richer in oxygen as the alloy became richer in nickel. The morphology of the magnetite precipitate changed markedly and probably was dependent upon the iron to oxygen ratio, but might have been modified also by changes in the traces of nickel dissolved in the wustite. For example, compare the needles of magnetite in Figure 4 with the cubes of magnetite shown by Himmel et al.[6]

There is a complete absence of hematite in these later studies.

### X-Ray

X-ray determinations qualitatively confirmed the metallographic observations and agreed with the earlier results when the residual traces of unstable phases were ignored. The data are summarized in Table 1. The almost complete absence of metallic particles in the outer scale makes it doubtful that they were completely in equilibrium. In this respect, the subscale was more reliable. Accuracy in lattice parameter determinations was limited by the relatively small amount of oxide produced in some cases and by the fact that the X-ray beam sampled only a few coarse grains in which the oxides seem to have grown with preferred orientations. Some diffraction lines expected in powder patterns were unusually faint. In any case, there seems to be no trend with distance into the specimen.

Another difficulty in interpretation of the X-ray data lies in the sparseness of data or discordant data on the alloys and oxides. The lattice parameters for face-centered cubic alloys determined by three groups of investigators[7] disagree with those given by Moreau.[2,8] The former are used here.

The wüstite lattice parameters of Willis and Rooksby[9] agree with those of Jette and Foote,[10] if the conversion factor for kX to Angstrom units is applied to the latter. Bénard's[11] results differ substantially from these.

Only for the extreme spinel compositions $Fe_3O_4$ and $NiFe_2O_4$ have lattice parameters been reported. Hickman and Gulbransen[12] gave a value for $NiFe_2O_4$ and Verwey and Haayman[13] determined the variation of lattice parameter with iron to oxygen ratio in magnetite. The fact that the cation to anion ratio and iron to nickel ratio can both vary appreciably in this phase, makes it difficult to be certain of interpolations. However, $a_0$ decreases with increasing oxygen to iron ratio in magnetite by a much smaller amount than the change associated with varying iron to nickel ratio. Although a parameter determined on powder taken from a single crystal ferrite[3] containing 18.12 weight percent Ni lies on the straight line connecting the extreme points in Figure 5, some of the values in Table 1 lie outside the range. The wüstite values are compared in Figure 6. Figure 7 gives the data for face-centered cubic Fe-Ni alloys. In each case the line used to evaluate the compositions by means of X-rays is indicated so that the reader may see the uncertainties involved.

### Chemical Analyses

The external oxides, separated mechanically from the substrate, were analyzed for average nickel content. The subscales were extracted with bromine

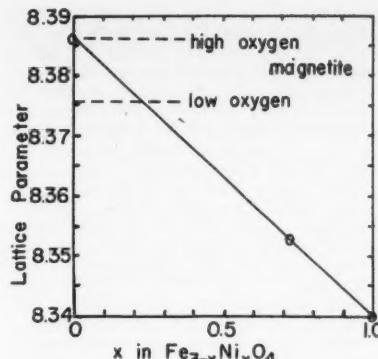(3) Purchased from the Linde Air Products Company.

Figure 5—Variation of lattice parameter in the spinel crystals with compositions between magnetite and nickel ferrite.



Figure 6—Variation of the lattice parameter with iron to oxygen ratio in wustite.



Figure 7—Variation of lattice parameter with composition in face-centered cubic iron-nickel alloys.



Figure 8—Iron-rich corner of the Fe-Ni-O system at 1050 C.

in methanol to dissolve the metal. Metal and oxide residue were analyzed separately for nickel. When two oxides were present in the specimen, the value obtained was an average for the mixture in whatever proportions existed. The results, given in Table 2, were not always reliable because of the small amounts of a particular product available in certain samples. The less reliable numbers are enclosed in parentheses.

In spite of the great difficulties in applying both chemical and X-ray analysis to these materials, it is evident that reasonable agreement exists in the few cases where reliable measurements are available from both sources.

## Discussion

*Phase Diagram*

From the results in Table 2, the three phase triangle should include an alloy composition above 50 percent nickel, a spinel composition containing about 10 weight percent nickel and a nickel-free wüstite containing 52.6 atomic percent oxygen. The only inconsistent result is the very low nickel concentration in the spinel of run 19 which was in contact with a very high nickel alloy. This contradicts several results[1] and probably is in error for an unknown reason. The alloy concentration seems to be the most inexact value of this set. Runs 17 and 18 indicate 51 and 65 weight percent nickel, while earlier results indicated 53 and 57 weight percent nickel. In the absence of a strong reason to eliminate any of these, the average is plotted at 55 atomic percent nickel. The spinel composition corresponds to $Ni_{0.4}Fe_{2.6}O_4$. The phase diagram is given as Figure 8.

*Scaling*

Bénard and Moreau[14] have measured oxidation rates for nickel alloys containing 30 percent or less nickel from 675 to 900 C. They found little nickel in the external scales with consequent enrichment of nickel in the underlying metal. Because of the relatively slow diffusion in the alloy, the concentration of nickel at the metal surface could go to very high values, dropping rapidly with distance away from the oxide layer. The rate curves could not be described by a simple relation. When fit to the equation

$$y^n = kt$$

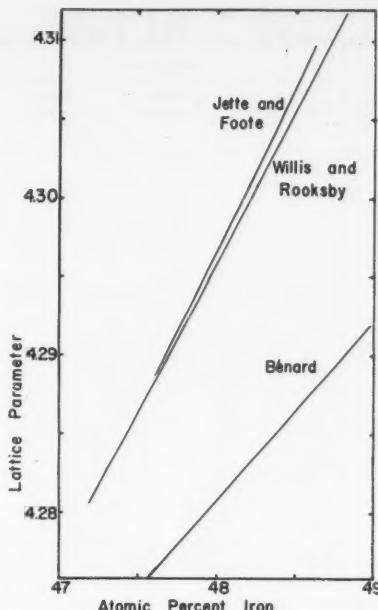it was found that n was greater than 2 in the early stages of reaction and lower than 2 in the later stages, except at

675 C. when a value of 2 applied reasonably well over the time of reaction.

Foley, Druck and Fryxell[3] studied 42 percent nickel alloys from 600 to 900 C and found no wüstite among the products. Again the alloy was found to be enriched in nickel just below the scale. They proposed that the growth rate of the scale was controlled by diffusion through the spinel layer. Presumably this would be mainly by cation diffusion,[6] but no evidence is in hand concerning the relative mobilities of iron, nickel and oxygen ions in nickel ferrite.

The mechanism to be proposed makes use of the observations outlined above and is consistent with these earlier suggestions. It simply seeks to tie them into a more comprehensive description.

Consider first an alloy which would be in equilibrium only with wüstite at temperature. When placed in a strongly oxidizing atmosphere, scaling would begin. No details can be given for the very early stages, for it is quite possible that an unstable phase nucleates most easily and then is replaced quickly by more stable materials. Surely wüstite will appear early and thereafter little nickel should reach the outer scale except when alloy particles are undermined in the subscale region and carried forward as more or less inert particles.

Because of the possibility of undermining subscale metal particles and the joining of subscale oxide particles to the external scale as oxidation proceeds, it is very doubtful that the inert marker techniques which are so helpful in studying oxidation mechanisms for pure metals will be of much unambiguous use in alloy oxidation studies. The more difficult procedure of measuring diffusivities in the oxides is indicated as a reliable course.

The strongly selective oxidation of iron will lead to nickel enrichment in the immediately underlying alloy layer. Oxygen solubility must be greater in the iron-nickel alloy than in pure iron in order for wüstite to precipitate farther back in the alloy as it does. This de-

pletes the iron content of the alloy still more. As nickel enrichment continues in the alloy, the equilibrium composition of the wüstite moves to a higher oxygen content, thus decreasing the concentration range for the wüstite layer. As a result, the driving force for diffusion decreases and the growth rate slows down more than the simple parabolic rate law predicts.[14]
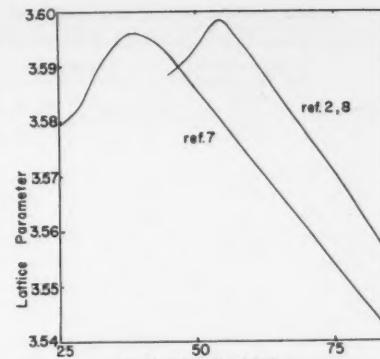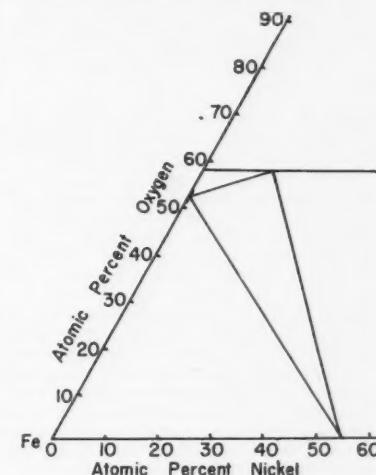
The fixed limiting concentrations from which this rate law is derived do not apply here. Furthermore, the subscale constitutes a substantial part of the oxide product. A simple mathematical picture cannot be constructed, and it is doubtful that a simple rate law should be anticipated.

Unless the initial nickel concentration is very low and diffusion in the alloy is able to halt the rise of nickel concentration in the alloy at the oxide interface, enrichment must inevitably drive the composition beyond that which is simultaneously in equilibrium with wüstite and spinel into the range where wüstite is unstable with respect to decomposition into alloy and spinel. How soon nucleation of spinel can occur is not clear. At this point there is no spinel in the subscale, and the external layer contains only magnetite nearly free of nickel which can remain in equilibrium with wüstite. Eventually the spinel forms in the nickel-enriched layer and begins to consume the wüstite from inside while the nickel-free spinel con-

**TABLE 2—Summary of Chemical Analyses and Comparison with X-Ray Results**

| Run | Composition Of Unoxidized Alloy Wt. Pct. Ni | Outer Scale | | Subscale | | |
|-----|-----|-----|-----|-----|-----|-----|
| | | Structure | Wt. Pct. Ni | Alloy Wt. Pct. Ni | Oxide Structure | Oxide Composition |
| 16..... | 37.13 | wustite + spinel | 8.72 | ...... | wustite + a little spinel | none detected |
| 17..... | 48.50 | spinel + a little wustite | 6.68 | 49.9 | wustite + spinel | much Ni in spinel* |
| 18..... | 48.50 | wustite + spinel | (3)* | ...... | wustite + spinel | much Ni in spinel* |
| 19..... | 48.50 | spinel only | (3)* | 85.5 | spinel only | (2.4)* |
| X-Ray Analyses........ | | Atomic Pct. Oxygen in Wustite | Wt. Pct. Ni in spinel | At. Pct. Ni in Alloy | At. Pct. Oxygen in Wustite | Wt. Pct. Ni in spinel |
| 17..... | | 52.7 | 5.1 | 51 | 52.6 | 10.6 |
| 18..... | | 52.6 | very low | 65 | 52.7 | 9.3 |
| 19..... | | none | very low | 89 | none | very low |

*Very small samples giving only approximate or qualitative results.

sumes it from the outside. Thus, the gradient in oxygen activity is maintained from outside to inside of the scale.

When the spinel and magnetite join, nickel can be delivered to the outer layer and a kind of homogenization may proceed. Whether the outer part of the overall spinel layer can ever catch up in nickel content cannot be estimated without a knowledge of the diffusion coefficients or direct analysis, neither of which are available. It may be that some nickel continues into the hematite layer.

It is shown here that even the spinel contains a higher iron to nickel ratio than the alloy with which it is in equilibrium. Therefore, nickel must continue to concentrate in the alloy phase. Wüstite, once eliminated, should not form again.

On pure iron, wüstite grows about twenty times faster than magnetite above 700 C. Thus it largely determines the overall growth rate of the composite oxide scale. When the wüstite composition range is narrowed by the presence of nickel in the metal phase a nearly proportionate decrease is to be expected in the oxidation rate at the start of the reaction, with further decrease resulting from the nickel enrichment just below the scale. Qualitative observations in the course of the earlier study[1] showed that even in a 2 percent nickel alloy the scaling rate was appreciably less than that for pure iron. If the nickel containing spinel has a growth rate about like that for magnetite, a twenty-fold reduction in the oxidation rate should result from the complete elimination of wüstite as one of the products.

In order to know whether further large improvements can be made, it is imperative that the mechanism of diffusion in spinels be understood, especially with regard to the effect of changes in the chemical nature of the cations on the diffusion processes which can support spinel growth. Such studies are under way in this laboratory and elsewhere. Recent work[15] has shown that it is important for the oxide to have sufficient plasticity to adjust to the retreating metal interface as growth proceeds. Whether changes in the nature and concentrations of cations in spinel crystals which affect the diffusivities will have a proportionate or stronger effect on the plasticities also may be a determining factor.

It seems clear that no simple rate law should be expected to hold over a range of times which includes a disappearance of one of the initial products of the reaction. Since Bénard and Moreau reached this condition for a 20 percent nickel alloy only after about 9 hours at 850 C it may be that some runs, especially at lower temperatures, have not gone this far.

Much has been written[16] about protecting metals from oxidation by alloying them with an element which is oxidized preferentially to form a surface layer which is dense, adherent, slow-growing and impervious to the base metal ion. The use of noble metal diluents has been considered theoretically[17] and experimentally.[18] The mechanism outlined above has more in common with the latter, for nickel oxide has a dissociation pressure greater than that of magnetite over the whole temperature range in question. NiO could form only near the outside of the scale to which sufficient nickel is never delivered. However, there is at least one new feature here. The presence of the alloying element has rendered the fastest growing phase thermodynamically unstable. The oxidation rate drops below that for either of the pure constituents in this case. The overall rate is determined by an entirely new phase. The improvement is potentially very great where the multilayer scales make a protective mechanism of this type possible.

## Summary

Iron-nickel alloys of several compositions were oxidized in oxygen at 1050 C.

Subscale formed preferentially at grain boundaries. Equilibration under an inert atmosphere occurred mainly by dissolution and diffusion of oxygen in the alloy phase. Porosity developed in the subscale region during equilibration, then began to sinter out on longer heating.

Several features of the iron-rich corner of the ternary phase diagram were determined. The three phase triangle was shown to have apices near 55 weight percent Ni in the alloy phase, 52.6 atomic percent oxygen in the wüstite phase, and 10 weight percent Ni in the spinel phase. Ni is virtually absent from the wüstite phase. Consequently the wüstite in equilibrium with an iron-nickel alloy has a higher oxygen content (lower iron activity) than when in equilibrium with pure iron at the same temperature.

The reduction in the concentration difference between the extremes of the wüstite layer on an iron-nickel alloy as compared with one on pure iron (with an overlying layer of magnetite in each case) leads to a lower growth rate of the wüstite phase on the alloy. By reference to the relative rates of growth on pure iron, it is anticipated that the elimination of wüstite as a stable phase should lead to a decrease in the overall oxidation rate by a factor of about 20, the actual rate determined by the growth of the spinel phase.

## Acknowledgments

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# Controlling Corrosion In Coal-Chemical Plants*

By C. P. LARRABEE and W. L. MATHAY

## Introduction

THE CONTROL of corrosion in a coal-chemical plant, as in any chemical plant, is dependent upon proper consideration of the various environments, the process conditions, and the economic factors. The purpose of this discussion will be to (1) review the protection of structural-steel work, roofing, and siding by paints, from the standpoint of minimizing maintenance costs, (2) present data showing the types of constructional materials that are resistant to the many corrosive conditions encountered, and (3) discuss the mitigation of corrosion through the proper selection of materials and changes in process conditions. Corrosion by atmospheres, by coal, and by chemicals is surveyed in somewhat of a general manner. From time to time during the course of this presentation, a brief description of the process as it concerns certain pieces of plant equipment will be necessary.

## Corrosion by Atmospheres

### Outside Structural Steel Work

Because local atmospheric corrosion at most coal-chemical plants is severe, considerable thought should be given to the economic maintenance of the present installations and to the design and protection of new ones. Frye[1] has described some of the various types of paints that are suitable for such installations. The service life of a paint film is dependent upon the atmospheric corrosion resistance of the steel to which the paint is applied;[2] therefore, a study should be made on the economics of using structural copper steel, or the even more corrosion-resistant high-strength low-alloy steels for new construction.

### Roofing and Siding

Because of the extensive use of corrugated steel roofing and siding, this discussion will be limited to materials capable of being corrugated. The most vulnerable portion of this type of roofing is the area where the ends and a few inches of the sides of one sheet are lapped over the ends and sides of adjacent sheets. The skyward surfaces of roofing and of most siding are periodically washed by rain which removes any accumulated corrosive chemicals. However, contaminated condensation frequently drains down the interior sides of roofing sheets and keeps the lapped joints moist. Thus, adequate protection of these areas by painting before erection is very important inasmuch as periodic repainting is impossible.

In U. S. Steel's coal-chemical plants, the choice of roofing sheets usually lies between galvanized steel and some grade of stainless steel. Both surfaces

Mathay          Larrabee
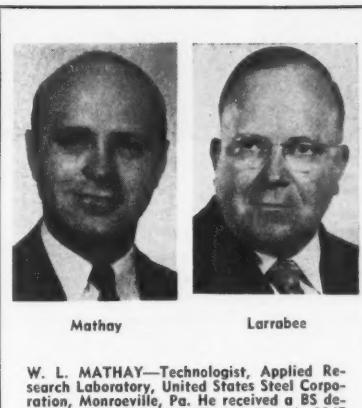
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of the galvanized sheets must be painted, whereas the stainless-steel sheets usually need be painted only on those surfaces that are not washed by rain. Because of the comparatively large buildings required to store the necessary quantities of sheets while hand-brushed paints are drying, it has been found more economical to paint and bake corrugated roofing sheets on a continuous production line. Thus, it frequently is more economical to paint both sides of stainless-steel sheets on a "paint line" than to paint certain areas only by hand.

It has been found that high labor costs economically justify the installation of roofing sheets that will last the expected life of a building. Only by studying the history of roofs on buildings that have been exposed to similar environments can one decide which of the several types of roofing sheets to select. For buildings such as store

## Abstract

Data are presented showing the types of constructional materials that are resistant to the many corrosive environments in coal-chemical plants. The protection of structural-steel work by paints is viewed from the standpoint of minimizing maintenance costs. To minimize the corrosive attack, copper steels and high-strength low-alloy steels are frequently used for outside structural-steel work, and stainless steels are used for roofing and siding applications.

Coal-handling equipment, and processing equipment such as primary coolers, tar stills, and light-oil stripping-stills are discussed with regard to the mitigation of corrosion through the proper selection of materials and changes in process conditions. Stainless steels such as AISI Types 304 and 316 were found to be economically resistant to corrosive attack in primary coolers, ammonia saturators, tar stills and light-oil recovery equipment, but should be used only in locations where plant corrosion tests have shown the use of these steels to be justified.                              8.8.1

houses having little or no atmospheric contamination in the interior, and in which some insulation is wanted, a sandwich-type roof is effective. Galvanized sheets (unpainted or painted, as desired) on the interior, insulating material in the center, and an outside sheet are a good combination. The composition of the outside sheet should depend upon the environment and the expected building life. Such 3-layer construction permits the satisfactory use of a material with less corrosion resistance than is necessary for single-sheet roofs because there is little or no condensation on the interior surfaces.

It is obvious from the above that each roofing application must be studied separately. The decision as to the best type of roofing for the most economic service during the entire projected life of the building should be based upon a consideration of all the factors involved.

## Corrosion by Coal

### Coal Bunkers

Most coals contain some sulfur in the form of pyrite which, upon contact with water and oxygen, oxidizes to ferric sulfate.[3] Depending upon the fineness of the coal, a few weeks to three months are required for this reaction to produce very corrosive conditions. The attack on carbon steels by ferric sulfate is severe; however, steels containing 12 percent or more of chromium are practically immune to attack. Thus, for coal bunkers, AISI Type 410 (11.5-13.5 percent Cr) stainless steel is the ideal constructional material.

### Coal Chutes

The corrosion rate of carbon steel immersed in water that is saturated with air decreases markedly with time. The corrosion rate for the first hour is about 250 mils (0.25) inch per year; for the first month it is 11 mils per year, and for the first year about 4 mils per year. When used under moist conditions, and

Galvanized Steel Tube     Copper Lined Steel Tube     AISI Type 304 Stainless Steel Tube
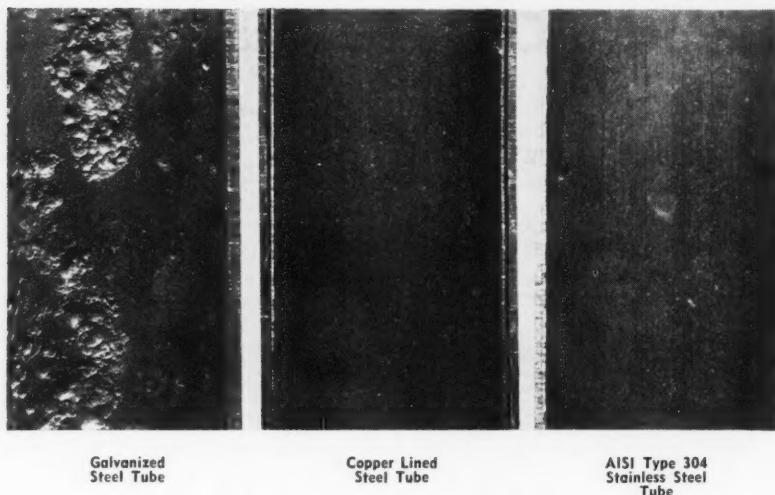
Figure 1—Sections of primary-cooler tubes after a 28-month exposure.

**TABLE 1—Corrosion of Primary-Cooler Tubes**

| MATERIAL | Compartment Number | Length of Service, Yr. | Wall Thickness, Inches | Maximum Pit Depth, Inches | Estimated Service Life, Yr. |
|---|---|---|---|---|---|
| Galvanized Steel | 1 | 2.3 | 0.120[3] | 0.080 | 3.5 |
| Copper-Lined Steel[2] | 1 | 2.3 | 0.035[4] | 0.009 | 13 |
| Type 304 Stainless Steel | 1 | 2.3 | 0.125 | None | Indefinitely Long |

[1] Water temperature 160 F.
[2] Lining was 99.6 percent copper.
[3] Exclusive of coating.
[4] Thickness of copper lining.

in locations where a protective rust film cannot form, carbon-steel or low-alloy steel equipment may have long-range corrosion rates approaching the 250 mils per year value. If steel equipment, such as a coal chute, is subjected to flowing moist water, a nearly rust-free metal surface that is continuously attacked by the corrosives in the coal, results. The attack is very severe even with freshly mined coal, and is higher if ferric sulfate has had time to form during storage periods.

Steels with more than 12 percent chromium do not depend upon built-up rust films to slow down or prevent attack by water or coal leachings. This explains why service tests have shown that Type 410 steel gives many times the life of carbon and low-alloy steels when it is used as the bottoms of coal chutes. High labor costs for replacement of carbon-steel or low-alloy steel parts, and loss of production through downtime, more than offset the initially higher costs of the stainless steels for this or somewhat similar installations. Service tests are necessary to determine the most economic steel, if previous experience does not do so.

## Coke Ovens

The coke ovens normally are not corroded to any extent because the exterior steel work exposed to the coal-chemical-plant atmosphere is usually warm enough to prevent condensation of moisture on the metal surfaces. The interior steel work, for the most part, is protected from the hot gases by silica brick.[4] Some attack on the carbon-steel

hoppers of larry cars, which are used to charge coal to the ovens, is experienced. Because these hoppers are subject to abrasion-corrosion by coal, the use of hoppers constructed of Type 410 has proved economical.

## Corrosion by Chemicals

### Primary Coolers

In primary coolers, the gases and vapors which were initially cooled in the "collecting" mains after leaving the coke ovens, are cooled from a temperature of about 200 F to a temperature of about 100 F. In the direct type of cooler, the gases are cooled by contact with "ammonia liquor," and in the indirect type by contact with metal tubes through which cooling water passes.

At one coal chemical plant, 30 indirect primary coolers, each having about 2700 galvanized-steel tubes, utilize a total of 40 million gallons of water per day. The insides of the tubes in the eight compartments of each cooler are exposed to river water treated with lime to raise the pH to about 4.5. Further treatment of the water, which is contaminated with acid drainage from old coal mines, is uneconomical because the water is not recirculated. Severe corrosion occurs on the interior surfaces of 2-inch galvanized-steel tubes that are in the four warmest compartments, where the water reaches a maximum temperature of about 160 F. The service life of tubes in these compartments is about 3 to 5 years, whereas in the other compartments the average life of the tubes varies from 10 to 15 years. Corrosion of exterior surfaces of the tubes is negligible.

Because it was believed that substantial savings in maintenance and replacement costs could be realized by using materials more resistant to corrosion than galvanized steel, a 3-phase corrosion-testing program was initiated. In the first compartment (hot-end) of a cooler, a service test of AISI Type 304 (nominally 18 percent Cr-9 percent Ni) stainless-steel tubes, copper-lined steel tubes, and galvanized-steel tubes was started. Concurrently, a corrosion-rack test was conducted to obtain information on the corrosion resistance of various constructional materials exposed to hot river water. Subsequently, to obtain heat-transfer data, two experimental heat exchangers, one with Type 304 steel tubes and one with galvanized-steel tubes were operated in parallel with the primary coolers.

The results of the service test are presented in Table 1, and those of the rack test are shown in Table 2. Figure 1 shows a center section of each type of tube at the end of the service test. It was estimated from the results of the service test, Table 1, that galvanized-steel and copper-lined steel tubes would have service lives of about 3.5 and 12.7 years, respectively. Type 304 steel tubes would apparently have indefinitely long service lives. These conclusions are in agreement with the results of the rack test, Table 2.

Examination of the Type 304 steel tubes and the galvanized-steel tubes, after removal from the plant coolers and from the experimental heat exchangers, showed that the stainless-steel tubes were practically scale-free, whereas the galvanized-steel tubes were heavily scaled. The average thickness of scale in the primary-cooler tubes is shown in Table 3. The heat-transfer data indicate that in the four warmest compartments of the plant coolers, Type 304 steel tubes, because of their nonscaling and nonrusting characteristics, will transfer up to 35 percent more heat than galvanized-steel tubes. Thus, the use of Type 304 steel tubes will permit a considerable reduction in the required number of tubes.

The first four compartments of the present primary coolers will be redesigned and rebuilt to afford maximum use of the advantages of Type 304 steel tubes. New primary coolers are also being constructed with Type 304 steel tubes in the warmest compartments. It is estimated that the use of Type 304 steel tubes will result in substantial yearly savings.

### Ammonia Saturators

After the coke-oven gas leaves the primary coolers, it is reheated prior to its entry into the ammonia saturators. The gas is bubbled through an aqueous solution saturated with ammonium sulfate and containing about 4 to 8 percent free sulfuric acid. Crystals of ammonium sulfate precipitate from the saturated solution, and are continuously withdrawn in the form of a slurry from the bottom of the saturator.[4] Chemical-lead linings, while still used in a number of saturators, are subject to mechanical failure as well as to localized corrosion and the abrasive action of ammonium sulfate crystals.

Pogacar and Tice[5] have presented the results of corrosion tests in ammonia saturators. Their data indicate that the most economical constructional material is Type 316 (nominally 17 percent Cr-

12 percent Ni-2.5 percent Mo.) The use of Type 316L (0.03 percent maximum carbon) in the saturators at the authors' company's plants has minimized corrosion and mechanical maintenance problems, and has permitted improved design and operation.

### Light-Oil Recovery Equipment

In the light-oil scrubbers the "light oil" is absorbed from the coke-oven gas by direct contact with a "wash oil." (Light oil contains benzol, toluol, and xylol plus minor amounts of other constituents, all of which have boiling points below 200 C.) The resultant mixture of wash oil and light oil is preheated as it passes through a series of heat exchangers prior to its entry into the light-oil stripping still. In the stripping still, the light oil is steamed-distilled at a temperature of about 284 F to 320 F, and subsequently cooled and separated from entrained wash oil and water. The wash oil leaving the bottom of the stripping still then passes through a series of heat exchangers for the recovery of latent heat and then passes to storage. From storage, the wash oil is returned to the light-oil scrubbers for the removal of additional light oil from the coke-oven gas.[4]

Most of the company's plants make use of a petroleum oil for this purpose, although a creosote oil (a coal-tar fraction) is used in one plant. At those plants utilizing petroleum wash-oil, only minor corrosion problems have been encountered in the light-oil recovery equipment. However, where creosote oil is used, both in this country and in Europe, severe corrosion problems have been encountered. Various investigators,[6, 7, 8] have attributed the corrosivity of creosote wash-oil to ammonium thiocyanate, and have pointed out that incomplete ammonia recovery from the coke-oven gas contributes to the formation of such corrosives in the oil.

Recently, at a plant utilizing the creosote wash-oil, corrosion failures of carbon-steel heat exchangers and pipelines in the wash-oil system occurred more and more frequently. Failures also were encountered in equipment constructed of Type 410 steel. (Some corroded portions of plant equipment are shown in Figures 2 and 3.) Both laboratory and plant investigations were undertaken to ascertain the causes of the severe corrosion, and to determine the design and process conditions required to minimize corrosive attack. The results of the laboratory investigation indicate that the presence of water and thiocyanate compounds (principally ammonium thiocyanate) in the wash oil is the major cause of the rapid corrosion of carbon-steel equipment, as shown in Table 4.

Preliminary results of plant tests indicate the same conclusions. One of the factors contributing to the corrosivity of the oil is its tendency to form emulsions with water. Water, which enters the wash-oil system as a result of condensation or of leakage, is difficult to remove by means other than distillation. The emulsified water, apparently associated with solids in the oil, can accumulate in the system and serve as a carrier for corrosive substances. The effect of the presence of water and thiocyanate compounds in creosote wash-oil on the corrosion of carbon steel is shown by the results of laboratory tests, Table 5. Furthermore, ammonia, if not almost completely removed from the coke-oven
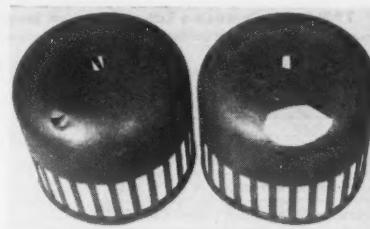


Figure 2—AISI Type 410 stainless steel bubble caps after a 1-year exposure in a light oil stripping still.

**TABLE 2—Corrosion-Rack Tests[1]**

| MATERIAL | Length of Exposure, Year | Corrosion Mils per Year |
|---|---|---|
| Type 302 Stainless Steel.... | 1 | 0 |
| Type 410 Stainless Steel.... | 1 | 3 (Pitted) |
| Admiralty Brass........... | 1 | 5 |
| Copper................... | 1 | 3 |
| Copper Coupled to Steel.... | 1 | 0.3 |
| Structural Carbon Steel.... | 1 | 39 |
| Structural Steel attached to Copper................ | 1 | 65 |
| Structural Copper Steel.... | 1 | 40 |
| Galvanized Steel.......... | 0.5 | 14[2] |

[1] Water temperature 160 F.
[2] Duplicate specimen lost at end of year.

gas, can react with sulfur and cyanide compounds to form additional corrosives.

Corrosion-rack tests were conducted in a light-oil stripping still to ascertain the resistance of various constructional materials to corrosion by the creosote wash-oil. The results of these tests, Table 6, show that Type 304 and 316 stainless steels were relatively unattacked.

On a basis of these findings, process changes were made to minimize the presence of water, ammonia, and corrosives in the wash oil and to prevent further contamination of the oil. Heat exchangers constructed of Types 304 and 316 were installed in place of corroded carbon-steel exchangers. Severely corroded pipe lines were also replaced with stainless-steel pipe. The light-oil stripping stills (carbon steel), which failed after about one year of service, were replaced with stripping stills constructed of Type 304. Since the institution of the process changes and the substitution of stainless-steel equipment for the carbon-steel equipment about one year ago, corrosion in the wash-oil system has been greatly minimized. It is believed that the substitution of stainless steel for carbon steel in certain critical pieces of equipment will ensure uninterrupted production during periods when ammonia recovery is not complete and when water pick-up by the wash oil occurs.

### Tar Stills

The tar that is removed from the coke-oven gas in the collecting mains is combined with the tar removed in the primary coolers. After dehydration, the tar is heated to a temperature of about 752 F in a tar heater containing Type 316 stainless-steel radiant tubes and carbon-steel convection tubes. The tar leaving the heaters enters the tar still, where it is fractionated into so-called carbolic oils, creosote, and pitch. The carbolic oils are further treated for the recovery of naphthalene, pyridine



Figure 3—Carbon steel nozzle after a 7-month exposure in a light oil stripping still.

**TABLE 3—Amount of Scale in Primary-Cooler Tubes[1]**

| MATERIAL | Compartment Number | Length of Service, Yr. | Average Scale Thickness, Inches |
|---|---|---|---|
| Galvanized Steel | 1 | 2.3 | 0.110 |
| Copper-Lined Steel[2]...... | 1 | 2.3 | 0.007 |
| Type 304 Stainless Steel..... | 1 | 2.3 | 0.003 |

[1] Water temperature 160 F.
[2] Lining was 99.6 percent copper.

"bases" (pyridine and its homologues), and tar "acids" (phenolic compounds).

The cast-iron bubble caps in cast-iron tar stills usually last about two years. The results of corrosion-rack tests conducted in one of these tar stills indicate that Type 316 would be a much more corrosion-resistant material. A service test of Type 316 bubble caps in the tar still is in progress, and after more than one year of exposure, the bubble caps show little evidence of corrosive attack.

The results of the rack tests are illustrated graphically in Figure 4, which also shows the percentage of inorganic chlorides in each tar fraction, as based on the chloride content of the material fed to the still. The most severe corrosion occurred near the center portion of the still where the temperature is about 482 F and where the concentration of chlorides is greatest. The corrosivity of coal tars is believed to be related to the presence of these chlorides (associated with small droplets of moisture in the tar) and to organic materials, possibly tar acids.[4, 9]

On the basis of the above results, two new Type 316L steel tar-stills will be constructed. In the tar stills, the use of Type 316L (0.03 percent maximum carbon) would be required to eliminate the effects of welding or improper heat-treatment. A stress-relieving treatment of Type 316L steel tar stills is desirable to minimize the dangers of stress-corrosion cracking.

### Pyridine Rectifier—Tar Plant

By far the greatest amounts of pyridine bases are recovered from the tar that is removed from the coke-oven gas prior to its entry into the saturators. The bases are usually recovered from the lower-boiling oils (so-called No. 1 carbolic oil) evolved during the distillation of the tar. The oils are washed with a caustic soda solution to remove tar acids, and then with 15 to 30 percent sulfuric acid to remove the pyridine bases. After the acid washing, water, naphthalene, and tarry compounds are removed by evaporation at temperatures of 176 to 212 F in a lead-lined steel rectifier.[4] The oil is then neutralized with
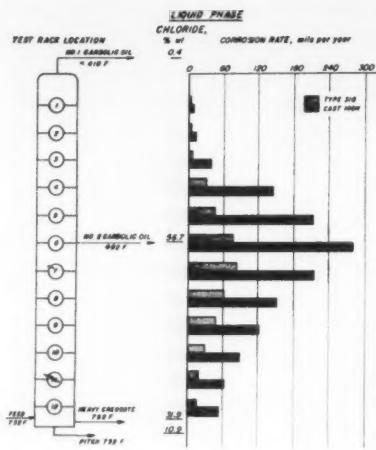
Figure 4—Corrosion of cast iron and Type 316 stainless steel in a tar still.

**TABLE 4—Corrosion Rate of Carbon Steel Exposed to Samples of Creosote Wash Oil[1]**

| ADDITIVE | Thiocyanate Concentration Grams per Liter | CORROSION RATE MILS PER YEAR | |
|---|---|---|---|
| | | Liquid | Vapor |
| None | .. | 16 | 9 |
| Ammonium Thiocyanate[2] (NH₄SCN) | 10 | 367 | 38 |
| Guanidine Thiocyanate[3] (CH₅N₃ · HSCN) | 10 | 184 | 30 |
| Quinoline Thiocyanate[3] (C₉H₇N · HSCN) | 10 | 15 | 21 |

[1] Temperature 320 F.
[2] Found to be present in creosote wash oil.
[3] May be present in creosote wash oil at times.

ammonia, and the pyridine compounds are recovered by azeotropic distillation with benzene followed by fractional distillation.

Corrosion-rack tests were conducted in both the liquid and vapor phases in the rectifier to ascertain whether materials other than lead could be used. The results of these tests, Table 7, indicate that chemical lead was considerably more resistant than the stainless steels.

## Conclusions

The atmospheric corrosion of carbon steel depends upon the environment. To minimize the corrosive attack, copper steels and high-strength low-alloy steels are frequently used for outside structural-steel work, and stainless steels are used for roofing and siding applications. However, the economics of using such materials must be determined by service tests.

Moist coal is very corrosive to carbon steel, but does not attack steels containing more than 12 percent chromium. Therefore, AISI Type 410 stainless steel has been found to be the ideal constructional material for coal-handling equipment such as coal bunkers and coal chutes.

Process waters and chemicals may cause severe corrosion of carbon-steel plant equipment. Stainless steels such as AISI Types 304 and 316 have been found to be economically resistant to corrosive attack in primary coolers, ammonia saturators, tar stills, and light-oil recovery equipment, but should be used only in locations where plant corrosion tests have shown the use of these steels to be justified.

To permit the proper selection of constructional materials, comprehensive corrosion-testing programs should be conducted. To be of the greatest value, corrosion tests must be conducted in full-scale plant equipment or in pilot-plant equipment under conditions simulating as nearly as possible those of production equipment. Laboratory testing may be necessary for controlled-variable corrosion tests.

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7. C. M. Cawley and H. E. Newall. The Corrosive Action of Benzol Absorption Oils. *Journal of the Society of Chemical Industry*, **64**, 285-290 (1945) October.
8. Ministry of Fuel and Power. Report on Investigations of the Benzol Technical Committee, 1942 to 1946, on Sludging and Corrosion in Benzol Absorption Plants. H. M. Stationery Office, 1947.
9. Roland Scott. Continuous Tar Distillation. *Chemical Trade Journal and Chemical Engineering*, **44**, 100-101 (1946) February 16.

**TABLE 5—Corrosion Rate of Carbon Steel Exposed to Samples of Creosote Wash Oil[1]**

| Thiocyanate Concentration, Grams per Liter | Water Content, Percent | CORROSION RATE, MILS PER YEAR | |
|---|---|---|---|
| | | Liquid | Vapor |
| 9 | 13 | 345 | 12 |
| 2 | 4 | 51 | 3 |
| 2 | 1 | 5 | 4 |
| 1.6 | 0.7 | 4 | 2 |

[1] Temperature 320 F.

## DISCUSSIONS

**Comments by J. M. Bialosky, Koppers Company, Inc., Verona, Pennsylvania:**

Coal tar may be dehydrated prior to distillation by decantation, which removes the water and the dissolved corrosive chemicals, or by heating, which removes the water but concentrates the salts in the tar.

Corrosion of wash-oil equipment is usually due to sulfur and cyanide compounds. The action may be accelerated by sludges which form by the polymerization of unsaturated cyclic compounds that are adsorbed in the oil. The polymerization is catalyzed by free sulfur formed by reaction of oxygen with sulfur compounds. Gas blanketing of storage tanks will minimize the oxygen in the oil.

**Reply by W. L. Mathay:**

We are fully in accord with Mr. Bialosky's comments.

**Question by R. McFarland Jr., Hill-McCanna Company, Chicago, Illinois:**

What is the mechanism for the corro-

**TABLE 6—Corrosion-Rack Tests in Light-Oil Stripping Still**

| MATERIAL | Rack Location | Corrosion Rate Mils per Year |
|---|---|---|
| Carbon Steel | Bottom of Still (Liquid) | 51 |
| Type 502 Stainless Steel | Bottom of Still (Liquid) | 40 |
| Type 410 Stainless Steel | Bottom of Still (Liquid) | 7 |
| Type 430 Stainless Steel | Bottom of Still (Liquid) | 2 |
| Type 304 Stainless Steel | Bottom of Still (Liquid) | 0.2 |
| Type 316 Stainless Steel | Bottom of Still (Liquid) | 0.2 |
| Carbon Steel | Top of Still (Liquid) | 118 |
| Type 502 Stainless Steel | Top of Still (Liquid) | 70 |
| Type 410 Stainless Steel | Top of Still (Liquid) | 3 |
| Type 430 Stainless Steel | Top of Still (Liquid) | 0.6 |
| Type 304 Stainless Steel | Top of Still (Liquid) | 0 |
| Type 316 Stainless Steel | Top of Still (Liquid) | 0 |

**TABLE 7—Corrosion Rate of Materials in Pyridine Rectifier-Tar Plant**

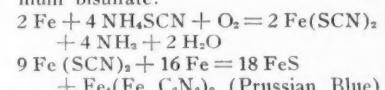| MATERIAL | CORROSION RATE MILS PER YEAR | |
|---|---|---|
| | Liquid | Vapor |
| Type 304 Stainless Steel | 79 | 25 |
| Type 304L Stainless Steel | 72 | 24 |
| Type 316 Stainless Steel | 50 | 8 |
| Type 430 Stainless Steel | * | 48 |
| Type 446 Stainless Steel | * | 35 |
| Lead[1] | 1.3 | 1.6 |

* Sample corroded so badly it fell from test rack.
[1] Lead specimen was typical of that used in this equipment.

sion of carbon steel by ammonium thiocyanate?

**Reply by W. L. Mathay:**

Cawley and Newall ("The Corrosive Action of Benzol Absorption Oils," *Journal of the Society of Chemical Industry*, **64**, 285-290 (1945), October), have proposed the following mechanism for the corrosion of carbon steel by ammonium bisulfate:

$$2\,Fe + 4\,NH_4SCN + O_2 = 2\,Fe(SCN)_2 + 4\,NH_3 + 2\,H_2O$$

$$9\,Fe(SCN)_2 + 16\,Fe = 18\,FeS + Fe_4(Fe\,C_6N_6)_3 \text{ (Prussian Blue)}$$

We belive that these reactions are essentially correct because we have identified the end products of the second reaction, ferrous sulfide, and Prussian Blue, in creosote wash-oil sludge.

# Heat Transfer Through Coated Metal Surfaces*

## By ROBERT P. LEE

### Introduction

PROTECTION of existing metal heat transfer surfaces against corrosion is a frequently encountered industrial problem. Applying a protective coating is an obvious solution in existing systems where corrosion inhibitors are not used. However, objections frequently are raised to coatings on the grounds that heat transfer will be decreased. For this reason it is desirable to know what effect coatings will have on heat transfer.

### Theoretical Considerations

The basic equation in the transfer of heat between two media which are separated by a wall is:

$$Q = UA (\Delta T_m) \qquad (1)$$

"U", the overall coefficient, in Equation (1) can be calculated by the use of empirical correlations[1,2] for determining the value of heat transfer coefficients of the films and the heat conduction through the uncoated metal wall.

If a coating is applied to a surface the effect is to add a deterrent to heat transfer along with the film coefficients and the heat conduction through the metal wall. The quantitative effect of adding the coating is calculable also.

The effect of application of a thin protective coating to a metal is small for low and medium coefficient heat transfer systems. Use of coatings for high coefficient systems will result in sharp drops in the amount of heat transferred. Examples of the various coefficient systems are:

Low: Gas to gas exchangers—Boiler economizers. Liquid to gas exchangers—Hot water radiators

Medium: Liquid to liquid exchangers—Coolers or heaters

High: Vapor to liquid exchangers—Steam heaters or condensers

### Experimental Procedure

In order to evaluate the effect of the application of a thin coating on a metal heat transfer surface, the apparatus shown in Figure 1 was constructed. The heat exchangers were simple double pipe types as shown in Figure 2. Hot, fresh water (inhibited with 2000 ppm sodium chromate) was pumped through the inside pipes and uninhibited fresh, cold water flowed through the annuli. The hot water was constantly recirculated, but the cold water was used only once.

Measurement of heat transfer coeffi-

**About the Author**

ROBERT P. LEE—Head of Corrosion and Materials Engineering Section of the National Lead Company, Titanium Division, South Amboy, New Jersey. He also has worked as Research Chemist and Development Engineer for the same company. Mr. Lee holds degrees from Polytechnic Institute of Brooklyn and Columbia University.

cients was desired. Equation 1, rearranged to

$$U = \frac{Q}{A (\Delta T_m)} \qquad (2)$$

which was used to measure the coefficients. A, the heat transfer area, is known. $\Delta T_m$, the log mean temperature difference, can be calculated from measured temperature values as follows:

$$\Delta T_m = \frac{(t_3 - t_2) - (t_4 - t_1)}{2.3 \log \frac{(t_3 - t_2)}{(t_4 - t_1)}} \qquad (3)$$

where:

$Q$ = Heat transferred, BTU/hour
$A$ = Area of wall normal to direction of heat measurement, sq ft
$\Delta T_m$ = Log mean temperature difference, degrees F
$t_1$ = Temperature of cold water into annulus, degrees F
$t_2$ = Temperature of cold water out of annulus, degrees F
$t_3$ = Temperature of hot water into pipe, degrees F
$t_4$ = Temperature of hot water out of pipe, degrees F

$Q$ can be calculated by:

$$Q = W (t_2 - t_1) \text{ or } Q = W (t_4 - t_3) \qquad (4)$$

where W is the water flow rate in lbs/hour.

The measurements were first made with the outside surface of one interior steel pipe coated with 4 mils of a baked phenolic finish. The other exchanger's interior pipe was also steel but was not coated. In this way meas-

### Abstract

Tests were conducted to determine what effect protective coatings would have on heat transfer of metal surfaces. Experiments involved the use of a 4-mil thick phenolic coating and a 15-mil thick vinyl coating on heat exchangers. It was found that application of thin coatings to such surfaces in low to medium coefficient systems, not only decreases corrosion but also gives higher heat transfer than ultimately experienced with corroded, uncoated metal surfaces. This is true even though a somewhat lower heat transfer coefficient exists initially for the coated surface. 7.4.1

urements were obtained for coated and uncoated steel surfaces at the same time.

The variations of the coefficients with time are shown in Figure 3. The uncoated pipe's coefficient decreased rapidly as a rust deposit built up on its outside surface. On the other hand the phenolic coated pipe's coefficient remained constant. The uncoated pipe's initial coefficient was higher than that of the coated pipe. However, after about three days the accumulating rust deposit had caused a decrease in the former to make both coefficients equal. The uncoated pipe's coefficient continued to fall rapidly to a value about half that of the coated pipe's coefficient. The constant value reached after eight days measurements on the uncoated pipe is attributed to equal rates of new rust formation and rust removal by the increased velocity of cold water flow.

A second, thicker coating (15 mils), a vinyl-aluminum type, was also studied. Results of these tests are plotted in Figure 4. The same heat transfer characteristics were noted. The initial uncoated coefficient was higher than the coated one. As was noted with the steel-phenolic unit the coated coefficient remained constant and the uncoated coefficient fell as rusting progressed
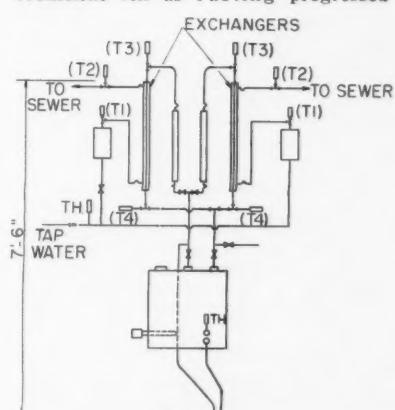


Figure 1—Apparatus used in evaluating the effect of the application of thin coatings on a metal heat transfer surface.
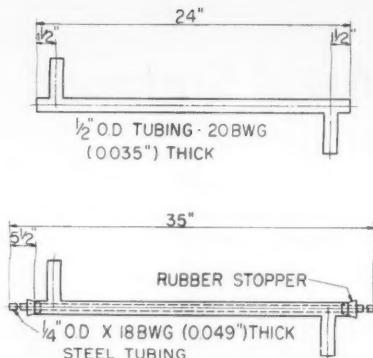
Figure 2—Double pipe type heat exchangers.



Figure 3—Variation of overall coefficient with time for coated (4 mils) and uncoated pipe.



Figure 4—Variation of overall coefficient with time for coated (15 mils) and uncoated pipe.

until it was lower than that of the coated one. The overall coefficient of the steel-phenolic system is higher than that of the steel-vinyl system. This is attributed to the decreased coating thickness (4 mils as compared to 15 mils for the vinyl coating.)

It was felt that the laboratory evidence warranted a field trial. Accordingly a field test was made in which a three coat* vinyl (without aluminum) system was applied to the water side of cast iron process liquid cooler. This is a low coefficient system due to the low water velocity used. Although no measurement of coefficient was made, the measured capacity of the unit was not

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* One primer coat (red lead), plus two top coats.

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decreased by the coating. Furthermore, life was increased indefinitely by periodic recoatings whereas serious pits had developed in one year prior to coating.

### Conclusions

Application of thin coatings to metal heat transfer surfaces, in low to medium coefficient systems, not only decreases corrosion but gives higher heat transfer rates than ultimately experienced with corroded, uncoated metal surfaces. This is true even though a somewhat lower heat transfer coefficient exists initially for the coated surface.

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2. Keyes and Deem. Chemical Engineers' Manual. John Wiley and Sons, Inc., New York, N. Y., 1942, pp. 8, 11.

### DISCUSSION

**Question by A. C. Levinson, Phillips, Texas:**

Have you done any work with ceramic coatings on thermowells for high tem-

perature application? What effect did the coating have on recorded temperature?

### Reply by Robert P. Lee:

Although no work was done it may be pertinent to comment that heat transfer at high temperatures, where ceramics are required, is not dependent on the mechanisms referred to in the paper. Radiation is a much greater factor.

### Questions by Robert E. Moore, Jr., Orange, Texas:

1. How would the heat transfer through a surface be affected by a calcareous coating laid down by impressing a high current density on the surface?
2. How would such a heat transfer coefficient compare with the coefficient of a corroded surface?

### Replies by Robert P. Lee:

1. Heat transfer would be decreased, probably in an amount proportionate to the coating's thickness.
2. No data are available.

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**Any discussions of this article not published above will appear in the June, 1958 issue**

# Reaction of Certain Chlorinated Hydrocarbons with Aluminum*

*By A. C. HAMSTEAD, G. B. ELDER and J. C. CANTERBURY*

## Introduction

ROUTINE LABORATORY studies were conducted in the mid-1930's to determine suitable materials for the storage and shipment of a large number of refined chemicals. In accelerated tests at the boiling temperature of the solutions it was observed that aluminum was sometimes attacked in a "catastrophic" manner by chlorinated chemicals such as carbon tetrachloride, the dichlorides of propylene and ethylene, and by the corresponding chlorohydrins of these unsaturates. The reaction was accompanied by liberation of heat and the evolution of large volumes of gaseous products. The corrosion product reacted vigorously with water.

Some of these tests were repeated with quite variable results. Detailed studies of the reaction were not made at that time to determine the reasons for the variable results, but it was recognized that a potential hazard existed in the use of aluminum for handling these chemicals.

In spite of the precautionary measures recommended as a result of the laboratory tests, reports have been received of aluminum inadvertently being used for handling propylene dichloride. In one important recent occurrence propylene dichloride was being handled in a Type 3003 aluminum line on a warm summer day. Work was discontinued in the early morning hours with the expectation that it would be resumed later in the day. For that reason the line was not drained. At 2 p.m. workmen nearby observed that the line was extremely hot and smoking. The abnormal condition of the line was reported immediately, but before the situation could be brought under control perforation occurred in many places releasing liquid and copious white fumes at high pressure that had developed inside the line from the corrosion reaction.

Fortunately, workmen attempting to prevent failure of the line were aware of its possible rupture and were properly protected so that no personnel injury or fire resulted. The line and all aluminum supporting structures in the immediate vicinity were corroded to destruction. The manner and extent to which the line was corroded is illustrated in Figure 1.

A time-sequence study of the propylene dichloride-aluminum reaction was made in the laboratory following failure of the aluminum line to illustrate the nature and rapidity with which this reaction may occur once conditions for initiation have been established. The reaction described for propylene dichloride is typical of that which has been observed for the other chlorinated hydrocarbons previously mentioned.

## Laboratory Test Procedures

Refined propylene dichloride of the following analysis passing commercial specifications was used in the tests:

| | |
|---|---|
| Specific gravity: | 1.1582 |
| Acidity, percent HCl: | 0.0002 |
| Cold test, degrees C: | OK |
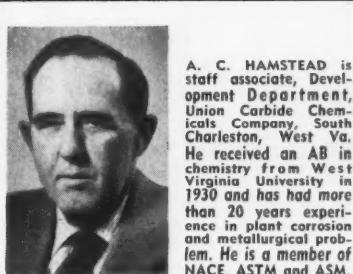
A. C. HAMSTEAD is staff associate, Development Department, Union Carbide Chemicals Company, South Charleston, West Va. He received an AB in chemistry from West Virginia University in 1930 and has had more than 20 years experience in plant corrosion and metallurgical problem. He is a member of NACE, ASTM and ASM.
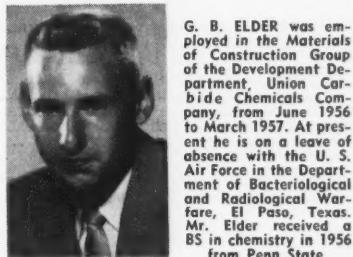
G. B. ELDER was employed in the Materials of Construction Group of the Development Department, Union Carbide Chemicals Company, from June 1956 to March 1957. At present he is on a leave of absence with the U. S. Air Force in the Department of Bacteriological and Radiological Warfare, El Paso, Texas. Mr. Elder received a BS in chemistry in 1956 from Penn State.
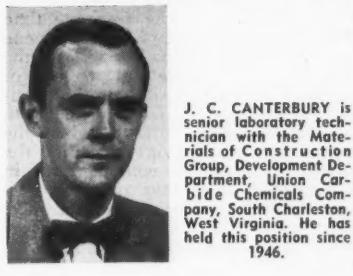
J. C. CANTERBURY is senior laboratory technician with the Materials of Construction Group, Development Department, Union Carbide Chemicals Company, South Charleston, West Virginia. He has held this position since 1946.

| | |
|---|---|
| Color, platinum-cobalt st'd: | 5 |
| Standard distillation @ 760 mm | |
| I.B.P. | 94.5 |
| 50 ml | 97.7 |
| D.P. | 97.5 |

The laboratory test apparatus is shown in Figure 2, and consisted of a 1-liter Erlenmeyer flask with ground-glass joint fitted with a 12-inch air-cooled and 12-inch water-cooled condenser.

Aluminum 3003 specimens 1-inch wide by 3 inches long by ⅛-inch thick were machined from standard mill sheet, cleaned, weighed on an analytical balance and suspended in the manner shown at three locations in the test apparatus containing 800-ml of the refined propylene dichloride. Heat was provided for the reaction by means of an electric hot plate. Significant changes in the appearance of the solution and test specimens were recorded and photographed in sequence from the time the temperature of the solution reached

## Abstract

A Type 3003 aluminum transfer line failed completely after only a few hours service in refined propylene dichloride. Following this failure a time-sequence study was made in the laboratory of the propylene dichloride-aluminum reaction to illustrate the nature and rapidity with which this reaction may occur once conditions for initiation have been established. Significant changes in the appearance of the solution and test specimens were recorded and photographed in sequence from the time the temperature of the solution reached the boiling point until the reaction had subsided sufficiently to remove the test specimens. Test specimens were reweighed at the end of the reaction and the corrosion rates calculated from the weight loss.

It has been found that chlorinated hydrocarbons have been handled successfully in aluminum under certain limits of product purity, time, temperature and condition of metal surface. It was recommended, however, that aluminum not be used as a material of construction for chlorinated hydrocarbons until these limits have been more clearly defined.

4.4.5

the boiling point until the reaction had subsided sufficiently to remove the test specimens.

The test specimens were reweighed at the end of the reaction and the corrosion rates calculated from the weight loss.

## Description of the Reaction

In less than six minutes after the boiling temperature was reached a sudden pink coloration of the solution developed. Following this discoloration, liquid which had collected along the edges of specimens exposed in the vapor space and condensate, began to effervesce and form black deposits with subsequent leaching of a dark brown liquid from the active metal areas which quickly discolored the entire contents of the test flask. Shortly thereafter, although the heat from the hot plate was turned off, the solution in the test flask began to effervesce vigorously and spill out the top of the condenser with considerable force along with dense white fumes having the odor of hydrogen chloride.

When effervescence subsided, heavy brown fumes were emitted from the top of the condenser (Figure 2). At the end of the reaction the test specimens were coated with a greasy black corrosion product and the remaining liquid in the flask was converted to a heavy viscous tar-like product.

## Discussion of Results

Stern and Uhlig[1] studied the corrosion of aluminum in boiling carbon tetrachloride, confirming the work of earlier investigators[2] that corrosion proceeds by direct chemical reaction yielding aluminum chloride and hexachlorethane as follows:

$$2\,Al + 6\,CCl_4 \rightarrow 2\,AlCl_3 + 3\,C_2Cl_6$$

They further demonstrated that an induction period or delay exists before the onset of attack. In later studies they proposed a mechanism of attack concluding that the reaction is initiated by the formation of active free radicals ($CCl_3^+$ and the complex $CCl_3^+[AlCl_4]^-$)

Figure 1—View of corroded sections of 4-inch OD aluminum 3003 transfer line after several hours service in refined propylene dichloride.
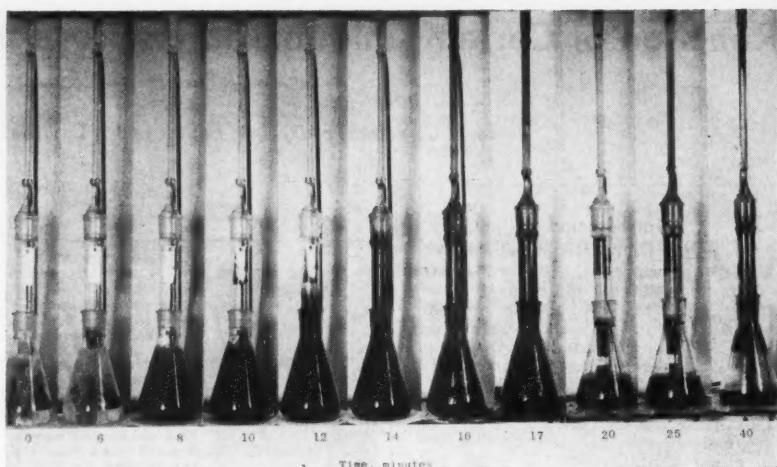


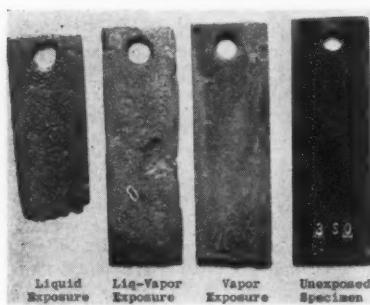| Liquid Exposure | Liq-Vapor Exposure | Vapor Exposure | Unexposed Specimen |

Figure 3—View of aluminum 3003 test specimens after 40-minute exposure in boiling propylene dichloride. At right is view of unexposed specimen of same size as those used in the test.



Figure 2—Time sequence photograph of the reaction between propylene dichloride and aluminum.

**TABLE 1—Corrosion of Aluminum 3003 in Boiling Propylene Dichloride**

|  | Completely Immersed | Liquid-Vapor | Condensate |
|---|---|---|---|
| Weight specimen, start, Grams | 16.6628 | 16.6902 | 17.7160 |
| Weight specimen, end, Grams | 6.6564 | 8.8860 | 11.6548 |
| Weight loss, Grams | 10.0064 | 7.8042 | 6.0612 |
| Average penetration in ipy | 281 | 227 | 176 |

NOTE: Test interval—40 minutes; Surface area of specimens—6.63 square inches each

taking prominent part in the chain reaction leading to the final corrosion products, aluminum chloride and hexachlorethane. The induction time by the boiling solution was found to be dependent upon the time necessary to remove oxygen from the solvent, the natural protective oxide film on aluminum, and the presence of corrosion product[3] ($AlCl_3$).

In nearly all respects the reaction of aluminum with propylene dichloride resembled that which has been described and reported by Stern and Uhlig for the carbon tetrachloride-aluminum reaction. However, once this reaction is initiated the rapidity of attack on the metal by propylene dichloride appears to be much greater than that described for the carbon tetrachloride-aluminum reaction.

Figure 1 shows how the 4-inch aluminum line was destroyed by corrosion within a few hours by attack from propylene dichloride. The consequences of such attack would have been much more serious had it occurred in the case of this chemical being stored in an aluminum storage tank, in aluminum river barges, or being transported on the highway in an aluminum tank truck.

Figure 3 is a view of the test specimens after a total exposure time of 40 minutes to the propylene dichloride-aluminum reaction. The specimen at the right in the photograph was not exposed in the reaction. This specimen was the same size of those that were exposed and is shown for comparison and to illustrate the rapidity with which the aluminum was corroded in the reaction. As a matter of theoretical interest, the actual weight loss of metal and corrosion rates calculated for the reaction time are given in Table 1.

Figure 2 is a photographic-time sequence of the reaction showing the initiation of attack at the 6-minute time interval along the edge of the specimens exposed to the hot vapor and in the condensate. The nature and progress of this attack is clearly visible on the specimens exposed in the condensate up to the 14-minute time interval when the reaction became so vigorous that the solution could not be contained within the test flask. Note that after effervescence of the test solution had subsided, heavy brown fumes were emitted from the top of the condenser (time intervals 20 and 25).

It should be emphasized that the induction period or time to onset of rapid attack on aluminum by the chlorinated compounds varies greatly. This period has been observed to vary from 16 to 120 hours in the case of boiling ethylene dichloride. In a test conducted a few days prior to the one reported herein, the induction period using the same propylene dichloride was 30 minutes for aluminum specimens which had been passivated by immersion in hot nitric acid and 45 minutes for specimens which had not been treated in this manner.

All of the chlorinated hydrocarbons mentioned are relatively unstable and show a gradual increase in hydrochloric acid content with time of storage. Until the investigations of Stern and Uhlig, it was the authors' belief that variations in results obtained were dependent primarily upon the extent of degradation of the chemical and to some extent on differences in the surface conditions or oxide film on the metal. However, no special attempts have yet been made to substantiate this belief, to explore the details of the chemical reaction, or to determine the limiting conditions under which this reaction may not occur. The results of the test, and experience cited

in the case of propylene dichloride, do indicate that the attack may be initiated with very pure chemicals at temperatures below the boiling point and within relatively short times, and that the protective oxide film on the metal surface does not perform a major part in delaying the reaction at the boiling temperature of the solution. The reaction described has not yet been observed with any of the chlorinated solvents at indoor room temperatures of the laboratory.

The authors' chief interest and concern in this reaction arises from the numerous inquiries received within the plant on the advisability of handling these chemicals in aluminum storage tanks, river barges, tank trucks and drums, and also from occasional reports received that these chemicals have been successfully handled in aluminum without incident. Variations encountered in the corrosion process, coupled with the fact that the metal appears to be unattacked at indoor ambient temperatures, makes it extremely difficult to accurately assess the suitability of aluminum for handling these chemicals. It appears that within certain limits of product purity, time, temperature, and condition of metal surface these chemicals may be safely handled in aluminum. So far as is known these limits have not yet been well defined. Until this has been done the authors prefer to pursue a safe course in advising against the use of aluminum as a material of construction for chlorinated hydrocarbons.

### References

1. M. Stern and H. H. Uhlig. *J. Electrochem. Soc.*, **99**, 381-389 (1952).
2. F. H. Rhodes and J. T. Carty. *Ind. and Engr. Chem.*, **17**, No. 9, 909-911 (1925).
3. M. Stern and H. H. Uhlig. *J. Electrochem. Soc.*, **100**, 543-552 (1953).

# A New Dynamic Test Facility For Aqueous Corrosion Studies*

By S. GREENBERG,* J. E. DRALEY* and W. E. RUTHER*

## Introduction

T HE DEVELOPMENT of water cooled nuclear reactors depends to a great degree on the availability of suitable corrosion resistant materials. Whenever the application involves the flow of coolant past a metal surface, testing can be done only in equipment which will provide suitable flow velocities.

Recirculating "loops" are useful for:

1. Demonstrating the suitability of components for operation in the given environment.
2. Studying the variables which affect corrosion.

The loop described here was built to provide maximum flexibility in accordance with the requirements of item 2.

There has been considerable operating experience with loops in which samples have been tested in continuously purified water. These have had serious limitations in the degree of control of solute concentrations, and it was chiefly

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° Argonne National Laboratory, Lemont, Ill.

to overcome this difficulty that the present facility was designed and built.

## Description of Loop

The design conditions are as follows:

Maximum temperature: 360 C
Maximum pressure: 3000 psia
Maximum flow rate: 20-30 ft/sec (depending on number of samples tested)

The loop is described by the flow diagram (Figure 1) and the accompanying parts list (Table 1). The circulating section of the loop is constructed of 1 inch O.D. Type 316 stainless steel tubing. The feed tanks are of Type 304L stainless steel. All joints are either welded or Swagelok fitting joints. The main source of heat consists of immersion heaters. Auxiliary heat is supplied by Monel sheathed resistance wire wrapped around the tubing at locations remote from the samples.

Solution is circulated past the test samples by means of a Chempump (to-

## Abstract

A new high pressure, high temperature dynamic aqueous corrosion test loop is described. Maximum design operating conditions are 360 C, 3000 psia, and 20-30 ft/sec velocity past test specimens. The design allows for greater flexibility of operation and more precise control of corrodent composition than had been obtained previously.          2.4.2

tally enclosed canned rotor type) centrifugal pump. To prevent boiling of the solution and cavitation in the pump it is necessary to maintain the pressure appreciably above the vapor pressure of the solution at the test temperature. For previous loops this has been accomplished by means of surge or pressurizing tanks heated to a temperature higher than that in the main circulating system. Since at the high pressures involved, the solubility of gases in water increases with increase in temperature, gas tends to migrate from the main circulating system to the surge tank. This makes precise control of gas content very difficult and necessitates frequent bleed-off from the surge tank.



Figure 1—High temperature and pressure aqueous flow corrosion test facility (flow diagram).

ALL FOUR LINES ARE IDENTICAL
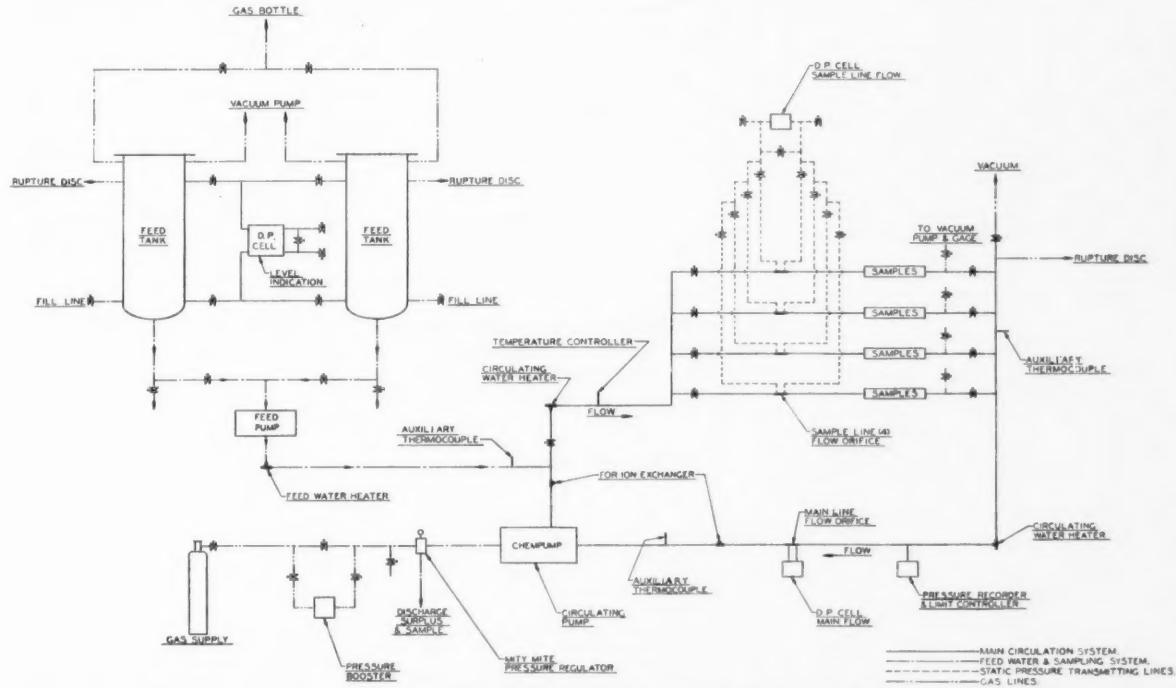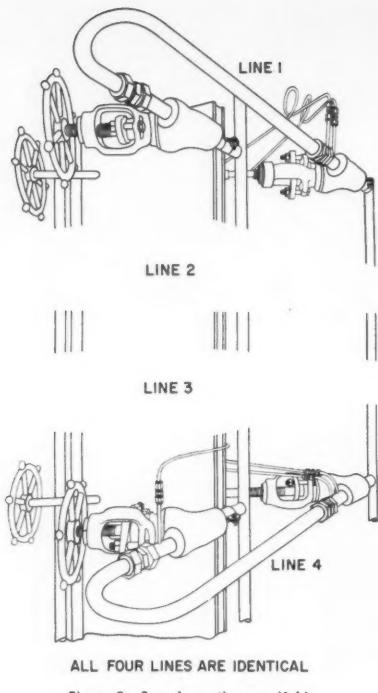
Figure 2—Sample section manifold.
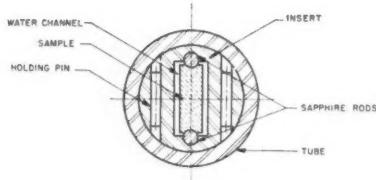


Figure 3—Sample mounting.

**TABLE 1—Loop Parts List**

| ITEM | DESCRIPTION[1] |
|---|---|
| Feed Tank | Fabricated at Rock Island Arsenal. Capacity: 42 gallons (each). |
| Vacuum Pump | Welch Duo-Seal Model 1402-B. |
| Rupture Disc Assemblies | Black, Sivalls & Bryson Safety Head Type ½-24 PS of suitable rating. |
| Feed Tank Level Ind. | Brown #792N7H4-B2 DP Cell Air Operated |
| 1″ High Temperature Valves (Circulating System) | Edward Valve #3924F |
| 1″ Low Temperature Valves (Feed Tanks) | Edward Valve #444F |
| ¼″ Valves (Instrument Lines, etc.) | Edward Valve #4152 |
| Feed Pump | Hills-McCanna Model UM-1F Single Stage Chemical Proportioning Pump (0.06 to 0.6 GPH). Maximum Pressure - 4500 psi. |
| Pressure Booster | Autoclave Engineers Model #HG15 |
| Back Pressure Regulator | #S-91-XW Grove Back Pressure Regulator (Mity-Mite) |
| Circulating Pump | Chempump Model CFHT-1½-1C-Special 20 GPM at 25 ft. Head |
| Flow Indicators | Foxboro Model #3AH-1 DP Cell of suitable range. Air operated. |
| Pressure Recorder & Controller | Foxboro Rotax Controller UR-13C. High and Low Pressure Cutoff. |
| Temperature Recorder and Controller | Leeds and Northrup Micromax |
| Temperature Indicator | Model 461-R Indicating Pyrometer (Assy. Prod. Co.) |
| Limiting Temperature Controller | West High Limit Gardsman Model JL |
| Immersion Heaters | Chromalox #RIS-755 or Watlow Firerod Cartridge Heaters Adaped for use with Swagelok Fittings. |
| External Heater Wire | General Electric Co. Heater Wire, Monel Sheathed. |
| Sample Insulators | Linde Air Prod. Co.-Synthetic Sapphire |
| Tubing Fittings | Crawford Fitting Co.-Swagelok Fittings |

[1] Where model numbers are given, it is not meant to imply that a similar piece of equipment produced by another manufacturer would not be as suitable. This list is given as a guide to those who might want to build similar equipment.

In the present loop, another system is used which also serves to maintain constant solution composition. Corrodent of the desired composition is pumped into the system from feed tanks by means of a positive displacement chemical proportioning pump. Fluid is discharged through a gas controlled back pressure regulator. Pressures above ordinary tank pressure (~1500 psi) are obtained by means of a pressure booster.

The capacity of the feed tanks is such that refilling is necessary only about once every four days. Control instrumentation makes it unnecessary to tend the loop except when loading or unloading samples or when test conditions are changed.

Four sample sections in parallel are connected to inlet and outlet manifolds by means of Swagelok unions (Figure 2). Sample sections can be removed or replaced while the system is at operating temperature and pressure. This greatly reduces down time and can eliminate the temperature cycling usually inherent when corrosion tests are to be run under the same conditions for varying lengths of time. Adjustment of valves allows simultaneous exposure of test samples to four different velocities. To avoid air contamination, each

individual sample section can be evacuated before being connected to the main stream.

Samples are mounted as shown in Figure 3. Synthetic sapphire rods prevent contact between the samples and the holder. If desired, sapphire rods also can be used to prevent contact between adjacent samples. Six samples plus two dummies (to prevent erosion effects up- and down-stream) can be loaded in each tube.

The loop has been operating since early April, 1957. During this time, operation has been continuous and trouble-free. The results of one corrosion test is the subject of a separate communication by one of the authors (WER.)

### Acknowledgment

# Statistical Concepts in The Testing of Corrosion Inhibitors*

*By C. C. NATHAN and E. EISNER*

## Introduction

CORROSION RESEARCH workers have long been familiar with the difficulties of obtaining reproducible data. Even under the most carefully controlled conditions of experimentation, wide variations are observed in weight losses, pit frequency, etc. of test coupons exposed in mildly corrosive conditions.

Mears[1] paper on the corrosion of mild steel by air and water at atmospheric temperature showed the statistical nature of rusting. Mears and Brown[2] and Aziz[3,4] extended this work to steel and aluminum. They point out that large statistical variations are expected under mildly corrosive conditions when local anodes and cathodes have average separations in excess of some critical distance (i.e., where the area of local cells exceeds a minimum area).

Large statistical variations generally are associated with intensified local attack, (i.e., pitting). Pitting is more pronounced the larger the critical area for maintenance of isolated anodes and cathodes. Thus, for very small critical areas attack will be general, and pitting will not be observed.

The critical area for pitting of aluminum is several orders of magnitude greater than for mild steel. This correlates with the well known fact that pitting failure in mild environments is much more pronounced for aluminum than for steel.

This paper deals with tests of various corrosion inhibitors for steel under attack by solutions of electrolytes in the presence of hydrocarbons. Such systems are of particular interest in the production of petroleum. Considerable work has been done in this field by NACE Group Committee T-1K. The concepts presented may be of interest to those considering other systems in which corrosion inhibitors are used.

Data are presented here for systems composed of hydrocarbons, aqueous electrolyte solutions and organic inhibitors. In these systems statistical variations in the weight loss and/or localized attack on mild steel test coupons are greater in the presence of inhibitors than in their absence.

The data are discussed using present theories of the mechanism of adsorption type inhibitors. Insofar as these statistical variations are concerned, mild steel in the presence of inhibitors may act much like aluminum in noninhibited

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E. EISNER—Theoretical Physicist, The Texas Company, Research and Technical Department, Exploration and Production Research Division, Bellaire, Texas. He received a BS from Brooklyn College in physics and mathematics and a PhD in theoretical physics from the John Hopkins University in 1944. He was subsequently employed at the Bureau of Standards and the Argonne National Laboratory. Dr. Eisner has been employed in his present position with The Texas Company since 1951. His main interests are in theoretical analysis and machine computations.

systems (i.e., the minimum area for local cell action on mild steel is greatly increased by the addition of inhibitors).

Such an hypothesis may be applicable to systems other than the oil-water systems described herein, since similar wide fluctuations are observed in testing of inhibitors on mild steel in other systems (e.g., gasoline inhibitors and rust preventives.)

## Experimental Work

### Static Test

The experimental work was carried out on two types of systems, classified as static and dynamic. Complete details of the static test have been described elsewhere.[5] This test was evaluated in a cooperative effort by a number of laboratories representing manufacturers, distributors, and users of inhibitors. The work was done by NACE Committee T-1K. Data were collated and evaluated

## Abstract

Workers in the field of corrosion testing have long been familiar with the difficulties in obtaining reproducible data. These difficulties are especially pronounced in mildly corrosive systems in which steel is being protected by corrosion inhibitors of the adsorption type. The present paper discusses tests on both synthetic fluids and actual fluids from producing oil wells. It describes the fluctuations in weight losses of test coupons and the occurrence of accelerated weight losses and increased differential attack or pitting in systems where low concentrations of organic adsorption type inhibitors are employed.

Data from both static and dynamic test systems are analyzed. In particular, the large amount of data collected by laboratories cooperating in the NACE proposed T-1K sour crude inhibitor test have been evaluated. The data are shown to approximate a normal distribution and are treated by methods of statistical analysis. Other systems are discussed in which normal distribution and other types of distribution have been observed.

An explanation is advanced for statistical variations in data obtained from these systems. The explanation is based on present knowledge of adsorption type inhibitors, surface heterogeneities on steel, and interaction between local anodes and cathodes.                5.8.1

at a meeting of the Committee at the South Central Regional meeting of NACE in Houston, Texas in October 1955. Preliminary results had been discussed previously.[5]

The test employs a mild steel coupon, one inch square, immersed for ten seconds in purified kerosene, then for seven days in a solution of 5 percent NaCl in water containing 500 ppm dissolved $H_2S$. The kerosene is first freed from all polar compounds by filtration through Fuller's earth, and the brine is freed from oxygen by purging with nitrogen. The inhibitors are dissolved in the phase in which they are soluble and tested at concentrations of 10 to 100 ppm based on total fluids.

The steel coupons are polished to a fine finish before testing and weighed to a tenth of a milligram. After exposure they are cleaned of corrosion products by standard methods, and again weighed. They also are roughly evaluated for frequency and depth of pitting, tubercles, etc. Inhibition is calculated as percentage of reduction in weight loss based on uninhibited coupons. All tests are run in replicate of two or more.

$$\varepsilon = 100 \ \frac{W_o - W}{W_o} \qquad (1)$$

where $\varepsilon$ = inhibitor efficiency, percent
$W_o$ = weight loss of uninhibited coupon (blank)

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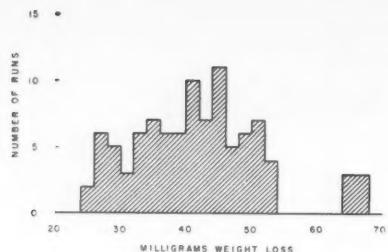
Figure 1—Distribution of blanks in T-1K test.
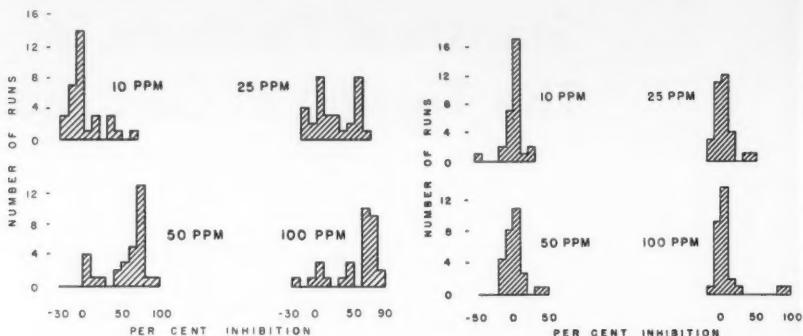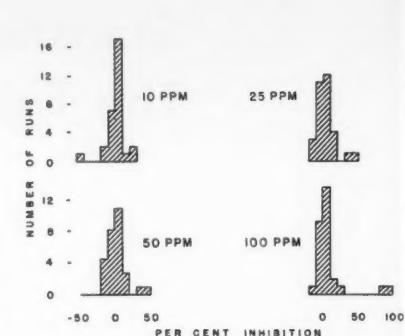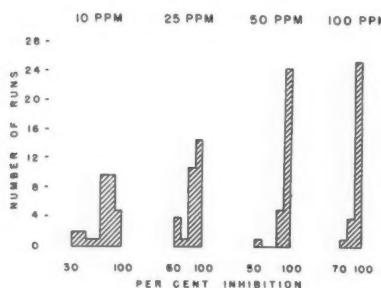


Figure 2—Percent inhibition obtained with varying concentrations of inhibitor No. 1.
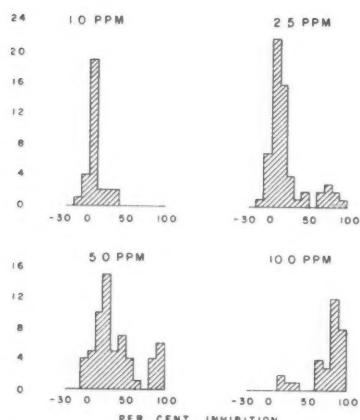


Figure 3—Percent inhibition obtained with varying concentrations of inhibitor No. 2.

$$W = \text{weight loss of inhibited coupon.}$$

The test was not designed to evaluate individual inhibitors in detail, but to screen promising materials from worthless ones. A screening is desirable because of the large number of materials used as corrosion inhibitors by petroleum producers or offered for use.

The data were gathered on samples of six coded materials sent out by the committee chairman. It was later revealed that two of the samples were merely diluted solutions of a third sample known both by laboratory and field experiments to be a very effective material even at low concentrations. Of the three remaining materials, one was a placebo, (i.e., known to be valueless in systems which the committee was studying.)

**194t**

**Four Inhibitors.** There were, therefore, four distinct inhibitors, referred to as 1, 2, 3 and 6, with 6 being the placebo. Seventeen laboratories participated in the test. The total number of runs was approximately 800, exclusive of the blanks run in the absence of inhibitors.

Every laboratory ran each of the original six samples at four inhibitor concentrations in duplicate, and reported percent inhibitions based on their own untreated blanks. The number of blanks run by individual laboratories was between two and twelve. Twelve laboratories reported sufficient data to allow the calculation of the mean square deviation from their average blank weight losses. These ranged from one to thirteen percent, averaging six percent over all of the laboratories reporting.

The variation of blanks from the grand average was much greater. Again based on the 12 laboratories, 89 blanks were reported. Individual averages gave blank losses between 32-68 mg with a grand average of 42.5 mg. The deviations of the individual averages from the grand average were from zero to 26 mg, and the average deviation of the individual averages from the grand average was six mg or 14 percent of the grand average.

The individual blank runs are shown as the histogram in Figure 1. The reproducibility in individual laboratories (6 percent) and between the twelve laboratories (14 percent) is quite good for corrosion work.

The reproducibility of data on inhibited systems in the static test presents an entirely different picture. Figures 2, 3, 4 and 5 present histograms for the four inhibitors evaluated by the test. The ordinate represents the number of runs having a percentage inhibition between the values shown on the abscissa. The group interval on the abscissa is 10 percent. Negative values of inhibition (i.e., acceleration of corrosion) are also plotted. There is considerable evidence that such accelerated corrosion can occur in these systems, and this point is discussed in detail in a later section of this paper. However, increased weight losses of only 10-20 percent above the blanks are probably of no significance, since this is hardly beyond the limit of reproducibility of the blanks themselves, as just pointed out.

**Findings From Histograms.** Examination of the histograms brings out the following points:



Figure 4—Percent inhibition obtained with varying concentrations of inhibitor No. 3.



Figure 5—Percent inhibition obtained with varying concentrations of inhibitor No. 6.

1. For a poor inhibitor (e.g., inhibitor 6), the data are sharply peaked around zero inhibition at all inhibitor concentrations. Only a small number of runs gave inhibitions differing by more than ten percent from zero.

2. For a good inhibitor at high concentrations (e.g., inhibitor 1 at 100 and 50 ppm), the data are sharply peaked at the interval 90-100 percent inhibition.

3. At lower concentrations of inhibitor 1, at concentrations of No. 2 between 5-10 ppm and at all concentrations of No. 3 (i.e., 5-50 ppm), the data are widely scattered. Since the scatter resembles normal Gaussian distribution, a random rather than a systematic cause of the scatter is indicated.

4. At very low concentrations of No. 2, (i.e., 2.5 ppm and below), the data are less scattered and cluster sharply around zero.

The data are summarized in Table 1 and plotted in Figure 6. The center of each vertical arrow represents the mean percent inhibition as given in the fourth column of Table 1, and the length of the arrow between the tip and center represents the standard deviation* of the mean as given in the fifth column of the table.

The solid lines represent the equation:

$$\varepsilon = \frac{\alpha c}{1 + \alpha c} \qquad (2)$$

This equation is of the same form as a Langmuir adsorption isotherm, if it is assumed that the fraction inhibition is proportional to the fraction of monolayer adsorption. Here, c is the concentration of inhibitor in ppm, and the value of $\alpha$ was selected for each inhibitor to provide a fit to the data.

For both Nos. 1 and 2, $\alpha$ is about 0.2; for No. 3 it is about 0.03; and for No. 6 it is zero. For systems which obey Equation (2) the larger the value of $\alpha$, the lower the concentration of inhibitor which is required to effect a given corrosion inhibition.

An equation of this form is used since there is a considerable amount of evidence which indicates that semi-polar organic corrosion inhibitors of the type here described adsorb to form mono-

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\* $\mu$ = standard deviation

$$= \sqrt{\frac{\Sigma_i \, (\varepsilon_i - \varepsilon)^2}{n}}$$

where:

$\varepsilon_i$ = percent inhibition of each run
n = number of runs

$\varepsilon$ = average percent inhibition = $\dfrac{\Sigma_i \varepsilon_i}{n}$

molecular films. This adsorption can often be represented satisfactorily by a Langmuir type isotherm; furthermore, the efficiency of the adsorbate as a corrosion inhibitor is often found to bear a direct relation to the amount of adsorbate. A number of papers on this subject have been published by Hackerman and his colleagues[6,7] and by others.[8,9]

The data are plotted in a different form in Figure 7. Here, $\mu$, the standard deviation from the mean value (the length of the arrow in Figure 6) is plotted versus the mean value of the fraction inhibition, $\varepsilon$ (the mid-point of the arrow in Figure 6). The points are fairly well represented by the parabola

$$\mu = 1.33\varepsilon(1-\varepsilon) \qquad (3)$$

**Spread of Data.** The maximum spread of the data is thus about 33 percent when the percent inhibition is 50 percent, and the spread becomes very low (i.e., 10-12 percent) when the percent inhibition is less than 10 or greater than 90. A spread of 10 percent or less in data would be of no significance since as was explained above this is about the order of variation which individual blanks give.

These findings are in line with a generalization familiar to workers in this field. It is easy to get reproducible data on inhibitors which are either very good or very poor; data for intermediately effective materials show such scatter that their use is questionable. It should be emphasized that the terms good and poor are relative, depending upon the concentrations employed. An inhibitor, such as No. 1, which appears to be good at concentrations of 25 ppm and above, might be a poor inhibitor at lower concentrations (see data for 10 ppm). Likewise, an inhibitor poor at low concentrations (No. 2 at 10 ppm and less) might be a good inhibitor at higher concentrations. Note that the same empirical line fits the data for inhibitors 1 and 2, so that actually these materials are equivalent. If used at the same concentrations, they therefore would be expected to give equal percentage inhibition (see data at 10 ppm.)

When the T-1K static test is employed, it is very difficult to rank inhibitors, because of the large fluctuations in the intermediate inhibition region. The concentration range giving from 10 to 90 percent inhibition should be investigated. If at the economic limit the 90 percent point has not been reached, the inhibitor may be discarded. The remaining inhibitors may be ranked by the cost required to attain 90 percent inhibition. Due to the large scatter of the data, this discrimination can only be coarse. The small scatter at high concentrations does not imply a sharp distinction between inhibitors because of the small sensitivity of inhibition to concentration in this region. (Note that the concentration scale of Figure 6 is logarithmic.)

In the absence of statistical variations in data, maximum differences in inhibitor efficiencies will occur at intermediate concentrations of the inhibitors, rather than where the inhibitors are most efficient.

If two inhibitors give $\varepsilon$ versus c data which can be represented by equations of Langmuir form,
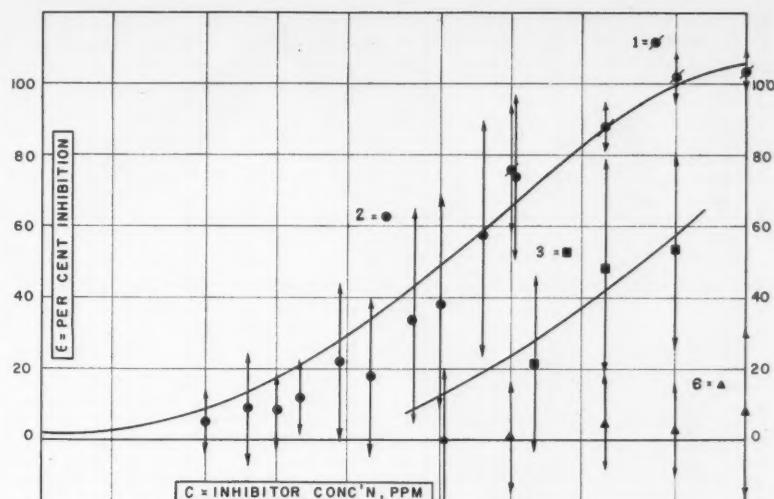


Figure 6—Percent inhibition obtained with varying concentrations of inhibitors 1, 2, 3 and 6.
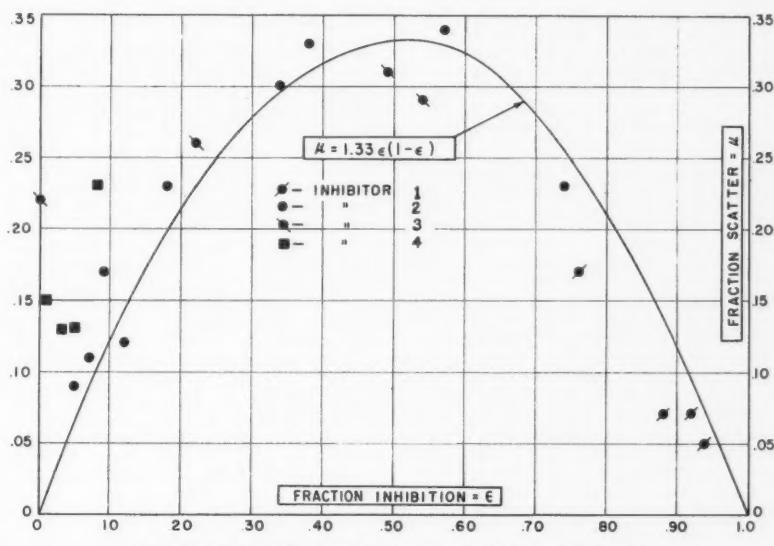


Figure 7—Fraction inhibiton vs fraction scatter for inhibitors 1, 2, 3 and 6.

**TABLE 1—Summary of Data From Cooperative NACE Inhibitor Tests**

| INHIBITOR | Concentration, ppm | No. of Runs | Mean Percent Inhibition | Standard Deviation of Mean, Percent |
|---|---|---|---|---|
| 1 | 10 | 30 | 76 | 17 |
| 1 | 25 | 30 | 88 | 7 |
| 1 | 50 | 30 | 92 | 7 |
| 1 | 100 | 30 | 94 | 5 |
| 2 | 0.5 | 30 | 5 | 8 |
| 2 | 0.75 | 30 | 9 | 17 |
| 2 | 1.0 | 30 | 8 | 11 |
| 2 | 1.25 | 30 | 12 | 12 |
| 2 | 1.825 | 30 | 22 | 23 |
| 2 | 2.5 | 60 | 18 | 23 |
| 2 | 3.75 | 30 | 34 | 30 |
| 2 | 5 | 30 | 57 | 34 |
| 2 | 7.5 | 30 | 57 | 34 |
| 2 | 10 | 30 | 74 | 23 |
| 3 | 5 | 30 | 0 | 22 |
| 3 | 12.5 | 30 | 22 | 26 |
| 3 | 25 | 30 | 49 | 31 |
| 3 | 50 | 30 | 54 | 28 |
| 6 | 10 | 30 | 1 | 15 |
| 6 | 25 | 30 | 5 | 13 |
| 6 | 50 | 30 | 3 | 13 |
| 6 | 100 | 30 | 8 | 23 |

Figure 8—Inhibition of hydrogen sulfide corrosion by cetyl trimethyl ammonium bromide.

$$\varepsilon = \frac{\alpha c}{1 + \alpha c} \text{ and } \varepsilon' = \frac{\alpha' c}{1 + \alpha' c}$$

$$\text{then } /\varepsilon - \varepsilon'/ = \frac{\alpha c}{1 + \alpha c} - \frac{\alpha' c}{1 + \alpha' c}$$

differentiating $/\varepsilon - \varepsilon'/$ with respect to c, equating the derivative to zero and solving for c, it is found that if $\alpha \neq \alpha'$

$$\text{then } c = \frac{1}{\sqrt{\alpha \alpha'}} \qquad (4)$$

is the concentration exhibiting greatest difference in inhibitor efficiency.

For example, it was stated above that the value of the constant $\alpha$ is about 0.2 for both inhibitors 1 and 2. Assume that $\alpha = 0.15$, $\alpha' = 0.25$. To obtain maximum differences in inhibition, one should compare the materials at a concentration, c, such that

$$c = \frac{1}{\sqrt{\alpha \alpha'}} = \frac{1}{\sqrt{0.15 \times 0.25}} \approx 5 \text{ ppm}$$

However, Figure 6 shows that a concentration of 5 ppm is unfortunately where the scatter of the data is maximum for these materials. In order to utilize effectively data gathered at concentrations in this range, it is necessary to employ statistical treatments based on the concepts of inverse probability. This treatment shows that the most effective region to investigate for the case shown is again the intermediate concentration region.

*Dynamic Tests, Synthetic Fluids*

The remainder of the experimental work was carried out in systems classified as "dynamic." The corrosive medium consisted of 100 ml of liquid and 30 ml of corrosive gas, either $CO_2$ or $H_2S$, above the liquid. The liquids were saturated with the gas at room temperature by bubbling the gas through the liquid for five minutes. A porous alumina bubbling tube was used.

The fluids were contained in a 5 oz polyethylene bottle. The test coupon was a soft steel strip, 2" x ½" x ¹⁄₁₆",

which had been machined from strip stock and polished with No. 240 carborundum paper on a metallographic polishing disc. The bottle was placed near the circumference of a wheel, two feet in diameter, which was rotated at six rpm. The wheel was surrounded by a thermostatted air oven, and the temperature was maintained at $120 \pm 2$ F unless otherwise stated.

Two sets of dynamic test conditions were used. The first used synthetic corrosive liquids. The aqueous phase was 90 ml of a brine which contained 10 percent NaCl, 0.5 percent $CaCl_2$ and 0.06 percent acetic acid. The oil phase was 10 ml of a neutral white oil. This oil had a distillation range of 525-635 F, and a specific gravity of 0.83. Its calculated molecular weight was about 200. The oil had no apparent metal wetting properties (i.e., the oil would not displace water from a water-wet steel coupon).

When the testing wheel was rotated, the steel strip was alternately immersed in the gas, oil phase, and aqueous phase. Inhibitor was added from stock solution to the test bottles before the inception of the test, and distributed itself between the two phases. A successful inhibitor always caused the steel coupons to pick up an oily layer which protected them from attack by the corrosive aqueous phase. The converse was not true. Sometimes, a coupon would be coated with a water-repellent layer, but when the coupons were cleaned of oil and corrosion products, pitting and other defects would be observed in the metal.

**Oil Well Fluids.** Fluids from producing oil wells also were used as corrodents. These tests differed from the synthetic fluid tests in that the natural fluids were used in the same oil to brine ratios as were being produced by the wells. These natural fluids were saturated with $H_2S$ or $CO_2$ after the 0.06 percent acetic acid had been added.

All other details were the same as for the synthetic test.

The test time was normally of 64 hours duration, after which the metal coupons were cleaned of oil and corrosion products by means of household cleanser, inhibited hydrochloric acid, and an organic solvent such as petroleum ether. They were then rinsed in acetone, dried, and weight losses determined. The appearance of the coupons after exposure was noted, and the frequency and depths of pits evaluated qualitatively.

**Cetyl Trimethyl Ammonium Bromide.** Figure 8 shows the results of a number of test runs with the synthetic fluids saturated with $H_2S$. A pure sample of cetyl trimethyl ammonium bromide was used as the corrosion inhibitor. This material, in impure form, is similar to several commercial inhibitors used in petroleum production. The weight loss of untreated coupons in this test was approximately 50 mg/day, and duplicate runs checked within 10 percent of the total weight loss.

Each point shown on Figure 8 represents one run. It will be seen that an inhibitor concentration of several hundred parts per million (ppm) is required before an inhibition of 90 percent is attained. At this concentration the reproducibility of the data is quite good. At concentrations below 400 ppm, the data are quite scattered and the average inhibition decreases. Notice that at 50 ppm inhibitor concentration duplicate runs might give values between 85 percent inhibition and 25 percent acceleration of attack. At concentrations of inhibitor near 20 ppm, a danger zone exists, in which a decided acceleration of attack occurs. At concentrations down to 5 ppm the data are still spotty and accelerated corrosion may occur.

At concentrations of 500 ppm and above, the average percent inhibition drops off slightly. This may be due to the formation of colloidal micelles. This decreasing effectiveness usually is not important in practical considerations since such high inhibitor concentrations are not normally economical.

Data similar to those of Figure 8 have been obtained for other inhibitors. The same general features have been noted, although the maxima and minima in the curves may be displaced in either direction on the concentration scale, and either up or down on the inhibition scale. However, it has been found generally that: (a) the scatter of the data is minimum at the maximum percent inhibition and at zero percent inhibition, (b) the scatter is maximum at intermediate percentages of inhibition, and (c) often, but not always, there is a danger area in which accelerated corrosion rates are observed.

The appearance of the coupons usually follows the same trend. Blank runs give coupons which are attacked overall and uniformly. Well inhibited systems usually show no indication of non-uniform attack. However, in the critical ranges where the weight losses are not reproducible, the attack is usually very non-uniform. Coupons often are smooth in their entirety except for a few isolated pits which are much deeper and sharper than in the absence of treatment. This is particularly true on the edges

and corners of the test strips. These areas seem much more susceptible to differential attack than do the faces. This behavior is not unexpected, since the edges are cold worked without annealing during the preparation of the test coupons.

This differential attack is very important in consideration of an inhibitor for service in oil production. Practically all cases of failure observed in this service are due to localized failure in threaded areas, upset areas in tubing, etc. Very rarely does equipment fail through reduction of structural strength due to uniform reduction of dimensions of equipment.

It appears that the systems which are being considered here would be classified as "dangerous" by Evans[10] (i.e., anodic inhibitors used in insufficient concentrations in systems which are under cathodic control). Oil field brines range in pH from about 4.5-8.0, and are believed to be under cathodic control. Corrosion rates in these systems have been determined by measurements of hydrogen evolution rates as described by Scott and Rohrback.[11]

The organic inhibitors which are used are generally polar nitrogen, oxygen, or sulfur compounds. Early workers considered that these materials adsorbed as onium (i.e., ammonium, oxonium, etc.) ions at local cathodes; later evidence has pointed to adsorption at local anodes. Hackerman and Makrides[12] have postulated general adsorption. It appears that the action of these organic inhibitors is similar to that of chromate ion which is dangerous below concentrations of several hundred ppm dependent upon the system in which it is employed. The organic inhibitors also appear to be dangerous below concentrations in the range from 10-1000 ppm, varying with the specific inhibitor and the system in which they are used. Chromate ion has been shown to be an anodic inhibitor.[10]

### Dynamic Tests on Actual Well Fluids

Tests have been carried out on actual well fluids from a number of different fields, some producing sweet crude, others sour crude. The fluids from the sweet systems were gassed with $CO_2$ and the sour ones with $H_2S$. There are

wide fluctuations in the rates of attack on untreated coupons, weight losses varying from only one to as much as 100 milligrams per day. However, the majority of fluids from untreated corrosive wells give weight losses between 10-50 mg/day, and the reproducibility of the data is normally satisfactory. When six blanks are run, the average deviation from the mean is usually within 15 percent. There are outstanding exceptions which will be covered later.

Because of the large number of commercial inhibitors which are offered to petroleum producers, it is necessary to screen those which are applicable for a certain field from those which are not. It has not been found possible to set up an order of rank for various inhibitors so that one series of evaluations will be applicable to all fluids. An inhibitor which is superior to a number of competitive products in one test fluid may be very inferior in another.

**Calculation of Inhibitor Cost.** In general, the observations just discussed under synthetic fluids are equally applicable for actual well fluids. Normally, inhibitors are not evaluated in actual well fluids at concentrations of over 100-200 ppm, because of cost of the inhibitor. As the percentage oil in the production decreases, the amount of inhibitor which can be economically used decreases accordingly. A simple rule for use in this connection is given below:

$$\text{Cost per bbl. oil} = \frac{\text{ppm inhibitor based on total fluids}}{\text{percent oil in fluids}} \text{ (cents)}$$

(5)

This formula is based on an inhibitor cost of $2.35 per gallon, an average figure for most materials used in oil production, and can be corrected for other costs. Costs of corrosion prevention of more than ten cents per barrel of produced oil are rarely justified; oil percentages of less than ten are not uncommon. Thus, there are many cases in which inhibitor treatments of less than 100 ppm will be necessary.

Table 2 presents data for evaluation of a number of commercial inhibitors in a sweet crude system consisting of 95 percent brine and 5 percent oil. Of nine inhibitors listed, seven show accelerated corrosion at 20 ppm. At 50 ppm, the situation improves and at 100 ppm all but one of the materials (Inhibitor D) could be considered satisfactory. At 50 ppm materials A, C, E, and F probably would be satisfactory. Notice that this is already a cost of 10¢ per barrel oil and that a lower concentration than 50 ppm would be dangerous.

Table 3 shows the effect of testing three inhibitors in two sweet oil systems, each containing 95 percent brine. The percent inhibitions are averages of

two duplicate tests. It can be seen that in Smith No. 1 the best inhibitor is Z, while in Jones No. 2 the worst inhibitor is Z. Similar results have been obtained on sour systems.

In general the rate of attack of either sweet or sour well fluids is less than the rate when using the synthetic fluids previously described. Furthermore, the reproducibility of replicate samples is poorer, and the variation in mean values of rates between different systems is considerable. When using synthetic systems, the data for uninhibited fluids will usually be reproducible within 10 percent of the mean value for as few as four replicate runs. With actual fluids, reproducibility within 20 percent for six runs is considered good. Thus, a typical series of 24 replicate runs on an uninhibited sweet crude-brine system gave an average weight loss of 102 mg, with a standard deviation from the mean of 40 mg. Thus, the deviation from the mean was 40 percent.

**Weight Loss Distribution.** The distribution of samples is as shown in Table 4. These data were treated assuming normal distribution, and it was calculated that in a series of 24 runs, there would be a probability of 90 percent that the true average weight loss would lie within 15 percent of the calculated average of the 24 runs. This large a number of replicate samples is not ordinarily convenient to run. Using a smaller number of runs (e.g., six), the reliability of the data would be decreased. Thus, assuming the same Gaussian distribution, a series of six runs could be expected with a probability of 80 percent to give a mean value within 23 percent of the true value. (The reader is referred to standard works on statistics for explanation of these calculations). Data of even this reduced reliability would generally be considered adequate for corrosion work. The example given above is typical of the kind of information usually found in work with untreated well fluids.

Another type of distribution with very scattered data may be observed with well fluids being treated with amounts of inhibitor insufficient to provide adequate corrosion protection. As an example, 64 runs were carried out on a fluid from a well which had been under treatment for a short period of time with corrosion inhibitor. The weight losses of the coupons were as shown in Table 5.

These data have a distribution which is skew; thus, the most probable weight loss is between 2-4 mg, but the arithmetic average is 16 mg. It would be nearly impossible to attach any meaning to the average in this case. Notice that these data resemble the data gathered on the NACE static test at low inhibitor concentrations, or the data given for dy-

**TABLE 2—Inhibition Tests on Sweet Crude (5 Percent) and Brine (95 Percent)**

| INHIBITOR | Concentration, ppm | Percent Inhibition |
|---|---|---|
| A | 100<br>50<br>20 | 99, 96<br>96, 93<br>acc., acc.* |
| B | 50<br>20 | 76, 88<br>94, acc. |
| C | 100<br>50<br>20 | 95, 95, 97, 99<br>97, 94<br>acc., acc., 32, 43 |
| D | 100<br>20 | acc., 35, 93, acc.<br>acc., acc. |
| E | 50<br>20 | 97, 98<br>95, acc. |
| F | 50<br>20 | 95, 97<br>acc., acc. |
| G | 50<br>20 | 92, 73<br>acc., 92 |
| H | 50<br>20 | 78, 93<br>86, 98 |
| I | 50<br>20 | 85, 97<br>92, 98 |

* Accelerates.

**TABLE 3—Comparison of Three Inhibitors in Two Sweet Systems (95 Percent Brine, 5 Percent Oil)**

| FLUID | PERCENT PROTECTION WITH VARIOUS INHIBITORS | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | INHIBITOR X | | INHIBITOR Y | | | INHIBITOR Z | | |
| | 50 ppm | 20 ppm | 100 ppm | 50 ppm | 20 ppm | 100 ppm | 50 ppm | 20 ppm |
| Smith No. 1 | 86 | 59 | 96 | 97 | 62 | 95 | 94 | 88 |
| Jones No. 2 | 91 | 95 | .. | 92 | 85 | .. | 96 | Accelerates |

**TABLE 4—Weight Losses of 24 Coupons**

| Weight Loss of Coupon, mg. | No. of Coupons |
|---|---|
| 0— 20 | 1 |
| 21— 40 | 0 |
| 41— 60 | 1 |
| 61— 80 | 5 |
| 81—100 | 4 |
| 101—120 | 6 |
| 121—140 | 5 |
| 141—160 | 0 |
| 161—180 | 1 |
| 181—200 | 1 |
| Total | 24 |

**TABLE 5—Weight Losses of 64 Coupons**

| Weight Loss of Coupon, mg. | No. of Coupons |
|---|---|
| 0— 2 | 3 |
| 2.1— 4 | 14 |
| 4.1— 6 | 6 |
| 6.1— 8 | 3 |
| 8.1—10 | 4 |
| 10.1—12 | 1 |
| 12.1—14 | 3 |
| 14.1—16 | 4 |
| 16.1—18 | 3 |
| 18.1—20 | 3 |
| 20.1—22 | 2 |
| 22.1—24 | 1 |
| 24.1—26 | 0 |
| 26.1—28 | 1 |
| 28.1—30 | 4 |
| 30.1—32 | 3 |
| 32.1—34 | 1 |
| 34.1—36 | 1 |
| 36.1—38 | 0 |
| 38.1—40 | 3 |
| 40.1—42 | 0 |
| 42.1—44 | 1 |
| 44.1—46 | 2 |
| 46.1—48 | 1 |
| Total | 64 |

namic tests on synthetic fluids when testing in the range of dangerous inhibitor concentrations.

## Discussion and Conclusions

As mentioned earlier there is considerable variation in corrosivity of fluids from individual untreated wells when tested by the dynamic method. This is rather surprising despite the well-known variations in corrosivity of well fluids. Explanations of field variations have been based on differences in pH, temperature, fluid velocities, and water-oil ratios. For example a recent paper by Rogers[13] points out the need for evaluating down-hole pH when considering well fluid corrosivity. However, in the dynamic test here employed, variables such as temperature, fluid pH, partial pressure of corrosive gas, and fluid velocity are held constant. The nature of the oil and its ratio to brine are the only obvious variables remaining. What is to explain the variation in corrosivity and response to inhibitors of similar well fluids pointed out in Table 2 given above? Here the fluid ratios of oil to water also are the same for the two systems tested.

An additional factor postulated by Hackerman, et al[14] is the presence of natural inhibitors in the crude oil and/or brine. These materials are supposed to be polar or semi-polar organic compounds which influence the oil and water wetability for metals, and other properties of interest in petroleum production (e.g., stability of oil field emulsions).

A recent paper by Hatch[15] discusses the occurrence of nitrogen compounds in petroleum and points out that about a quarter of the total nitrogen content of petroleum is basic or amine nitrogen. Such materials are the very chemicals which are presently being used as corrosion inhibitors in petroleum production specifically, and in other branches of the petroleum and chemical industries as well.

The presence of such basic nitrogen compounds in petroleum in varying amounts and of varying composition in different crudes could explain the difference in corrosivity of different untreated well fluids. Their presence also could account for the wide variations in laboratory test results. If such materials are present in critical or dangerous concentrations, they would be expected to result in widely scattered laboratory data, just as do inhibitors in synthetic systems as shown in Figure 8.

### A Proposed Explanation of the Observed Statistical Variations

The large statistical variations are, thus, inherent in the problem. They do not arise from defects of the methods used. As previously discussed, $\mu$, the mean square deviation of the observed inhibition, $\varepsilon$, is proportional to $\varepsilon(1-\varepsilon)$.

This form suggests a simple explanation. If the surface can be divided up into N non-interacting areas, each of which has probability P of being protected and a probability of $1-P$ of corroding, then

$$\varepsilon = P \text{ and } \mu = \frac{1}{N} \times P \times (1-P).$$ This

may be verified in standard references on statistics, or checked by the method of characteristic functions. The model described leads to a Poisson type distribution. In view of the experimental relation, $\mu = 1.33 \, \varepsilon(1-\varepsilon)$ observed for coupons of 12 sq cm area, the non-interacting regions in the above model have an area of approximately 16 sq cm. It is clear that this far exceeds the area covered by an individual inhibitor molecule. However, such a situation arises if, when two unprotected regions (anodes) lie within a certain critical distance of each other, the start of a pitting reaction at one site suppresses the pit initiation at the other. This concept has been fully discussed by Mears and Brown as well as by Aziz in the references cited earlier.

P can be related to a simple mechanism of adsorption of inhibitor molecules on a metal surface at a rate dependent on their concentration in solution, c. In turn, these molecules re-evaporate or desorb from the surface at a rate dependent on the mutual interaction characteristics, $\alpha$, of the inhibitor and surface. This leads directly to the Langmuir type equation, $\varepsilon = \dfrac{\alpha c}{1 + \alpha c} = P$.

It seems that the picture thus far presented describes the situation at high inhibitor concentrations. At low inhibitor concentrations, visible pitting does not seem to occur but general attack takes place. In the low concentration range the reaction is known to be under cathodic control. The experiments cited (Mears and Brown) which report a critical area of .09 sq cm per pit presumably refers to this situation, since no inhibitors were present. One would not expect

that at the extreme of cathodic control, the critical area should match that at the extreme where anodes are rare (i.e., most anodes have been covered by adsorbed inhibitor). It might be noted that the corresponding area for aluminum seems to be about 20 sq cm. It appears, therefore, that mild steel surfaces in contact with low concentrations of anodic inhibitors resemble unprotected aluminum in their pitting characteristics.

The explanation of the basic cause of the differential attack probably is tied in with local inhomogeneities in the metal surface. These inhomogeneities correspond to variations in local surface potentials, energies, and rates of adsorption, etc. Such sub-macro variations are well-known and have been demonstrated by voltage profiles as well as measurements of adsorption rates onto metal surfaces. Measurements in the authors' laboratory of the adsorption of palmitic acid onto iron powder from benzene solution indicate differences in adsorption constants of fifty-to-one between portions of surface covered between 0.0-0.3 and 0.95-0.99 fraction mono-layer. Such differences in specific adsorption rate would correspond to differences in adsorption energies of about 2.5 Kcal or surface potential differences of about 100 mv. Variations in surface potentials of this magnitude are not extraordinary.

Differences in adsorption of radioactive lead and cobalt ions onto various areas of actively pitting aluminum have been described by Aziz.[16] Preferential adsorption occurred onto local cathodes.

In the laboratory of the present authors autoradiographs taken of steel strips which had been exposed to wet benzene solutions of radioactive polar materials, palmitic acid and cetyl dimethyl benzyl ammonium chloride showed that both materials adsorbed preferentially onto local anodes. The local anodes were determined by the ferroxyl test and/or by appearance of rust. It was not possible to show whether the materials adsorbed onto the local areas because these areas were anodic, or whether the areas became anodic after adsorption of the polar materials. Most evidence points to the former hypothesis.

There are few precise data on the distribution of pits, although it is generally felt that the distribution is random. A recent paper by Streicher[17] on the pitting of stainless steel indicates random distribution of pits in the systems investigated. He states: "The data obtained from 70 comparable runs on Type 304 stainless steel in 0.1 N sodium chloride solution fall on a symmetrical distribution curve. Efforts to reduce the tolerance limits by various methods of surface preparation, grinding, and pickling procedures, and by controlling the time between specimen preparation and testing were without success."

In other systems such as those reported by Mears and Brown[2] the pit distribution essentially follows a Poisson form. In those described by Aziz,[16] the distribution is more complicated than either a Gaussian or Poisson type. It may be concluded that because of the heterogeneous nature of the surface of steel and other industrial metals, non-uniform attack on these surfaces may be expected in certain environments. When the environment is not suf-

ficiently aggressive to "iron out" local differences in surface reactivity, marked differential attack may be expected. This differential attack will be evidenced by pitting and/or highy irreproducible weight loss data. In such cases of widespread variations the data must be analyzed by statistical methods before they can be of any value.

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**Any discussions of this article not published above will appear in the June, 1958 issue**

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## TECHNICAL PAPERS ON CORROSION WELCOMED

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# Cathodic Protection of Iron
# In the Temperature Range 25 C–92 C*

By G. R. HOEY* and M. COHEN*

## Introduction

A STUDY of the effect of temperature on the cathodic protection of iron is of practical importance in connection with the application of cathodic protection to domestic hot water tanks. Although extensive field investigation[1,2,3] of cathodic protection of hot water tanks using magnesium anodes has been carried out, no laboratory investigation has been reported in the literature. A study of the performance of magnesium anodes at higher temperatures is in progress.

## Experimental

The corrosion cell used in these experiments consisted of an iron cathode and a magnesium anode immersed in dilute aqueous solution. The iron cathode consisted of a black iron specimen, 1 inch in diameter and ¼ inch long with a drill hole 1/16 inch in diameter along the backface, contained in a rubber holder so that only one face was exposed to the solution. The rubber holder, molded from neoprene rubber, consisted of: (1) a cylindrical cup with inside diameter slightly less than 1 inch in order that it would fit snugly over the iron specimen, and (2) a rubber extension into which a steel rod, 1/16 inch in diameter and 6 inches long, was molded for electrical contact. A current was supplied through a magnesium anode made in a similar manner using magnesium specimens machined from pure magnesium extruded rod.

The cells were placed in a constant temperature oil bath regulated to within 1 degree C. Stock solution was stored in overhead glass carboys, and flowed through a calibrated capillary direct to the test solution at the rate of ¼ liter per hour. The test solution (½ liter) was maintained at a constant level by an overflow. The corrosion cells, of which about eight were studied at a time, were maintained at constant current by discharging a DC voltage supply (112.5 volt) through an appropriate variable resistance, a calibrated microammeter, and the corrosion cell.

Prior to each experiment the iron specimens were abraded on 0, 2/0 and 3/0 emery, degreased in CCl₄, cleaned in 6N HCl solution with 2 percent Rhodine 60, and weighed. After the experiment the specimens were cleaned as before and reweighed. The runs were from one week to 10 days duration.

Cathodic polarization curves for iron in 110 ppm NaCl solution were determined using a similar type corrosion cell with a silver: silver chloride probe electrode (thermal electrolytic type) as reference electrode. The potentials of

the iron specimen, prepared in the same manner as for weight loss measurements, were recorded on a Leeds and Northrup Micromax recorder. The applied current densities ranged from 70 μ amp cm⁻² down to zero current in steps of 10 μ amp cm⁻² or 5 μ amp cm.⁻² Each setting of the current was maintained for about 10 hours.

The corrosion products of the iron were analyzed by X-ray analysis.

## Results

The corrosion rates (mdd) of the iron specimens after 7 to 10 days immersion in 110 ppm sodium chloride solution for various applied current densities and temperatures are shown in Figure 1. Corrosion rates of iron specimens after 10 days immersion in solution containing both NaCl and NaHCO₃ for various current densities at 58 C are shown in Figure 2.

Typical potential-time curves for iron immersed in 110 ppm NaCl solution observed during the determination of a polarization curve are shown in Figure 3. Curve 1 was obtained for iron maintained at 70 μ amp cm⁻² without previous polarization. The specimen was previously polarized at 45 μ amp cm⁻² for Curve 2 and at 10 μ amp cm⁻² for Curve 3. Polarization curves for iron in 110 ppm NaCl solution at 25 C, 58 C, 75 C, 92 C, are shown in Figure 4. Two curves are drawn at each temperature—one through the maximum potentials observed at each setting of the current after several hours polarization and the other through the minimum potentials. Standard potentials of the Ag: AgCl; NaCl half cell at the various temperatures studied were calculated from data of Bates and Bower.[4]

Magnetite with traces of lepidocite were identified by X-ray analysis in the corrosion products of iron which had been immersed in solutions containing

## Abstract

The cathodic protection of iron was studied in the temperature range 25 C to 92 C. The limiting protective current density and the open circuit cathodic current density for iron in dilute NaCl solution goes through a temperature maximum at roughly 75 C. This is explained in terms of the effect of decreasing oxygen solubility at the higher temperature on the local cathodic reaction,

$$2H^+ + O_2 + 4e = 20H^-$$

Iron corrodes under cathodic control at room temperature, whereas at the higher temperatures there is a mixed cathodic-anodic control.

Cathodic polarization curves for iron in dilute NaCl solution were obtained in the temperature range 25 C to 92 C. Unsteady potentials were observed in the vicinity of the limiting protective current, whereas at higher and lower currents, steady potentials were observed. The current density at which the potential of the iron reaches −0.5 volt on the hydrogen scale gives satisfactory protection.

The nature of the corrosion products of iron is unaffected by temperature in the range studied.                    5.2.2

110 ppm NaCl at room temperature and 92 C. In addition to magnetite and trace quantities of lepidocrocite, trace quantities of goethite were identified in the corrosion products of iron which had been immersed in a soultion containing 50 ppm NaCl and 150 ppm NaHCO₃ at 58 C. Mg(OH)₂ was formed on the iron cathodes at cathodic current densities greater than the protective value.

## Discussion

The possible electrochemical reactions which may occur on the surface of a corroding specimen in aqueous solution in the presence of oxygen are:

$$2H^+ + 2e = H_2 \quad (1)$$
$$2H^+ + O_2 + 4e = 20H^- \quad (2)$$

at the cathodic areas
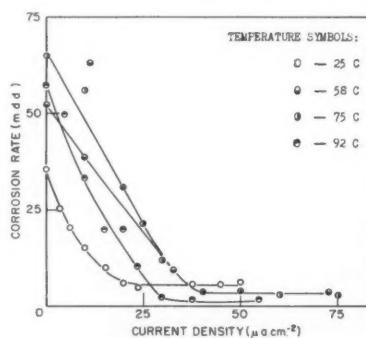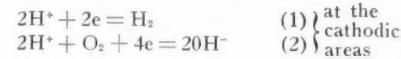


Figure 1—Dependence of corrosion rate of iron in a 110 ppm NaCl solution on applied current density. pH ranged from 9.0 to 9.5.
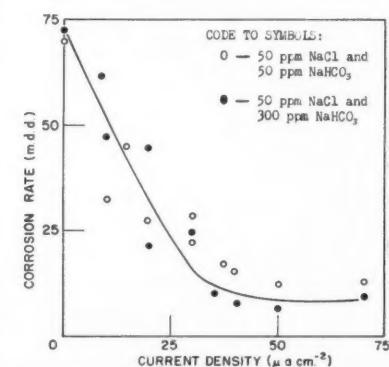


Figure 2—Dependence of the corrosion rate of iron at 58 C on the applied current density in solution containing NaCl and NaHCO₃, pH ranged from 8.5 to 9.0.
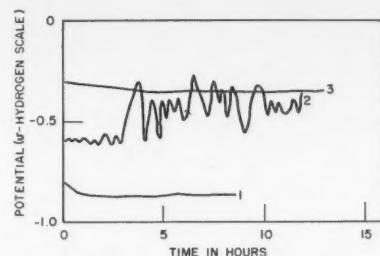
Figure 3—Potential-time curves for iron in a 110 ppm NaCl solution at 75 C, observed during the determination of a cathodic polarization curve. Currents for curves are as follows: Curve 1—70 $\mu$amp cm$^{-2}$; Curve 2—40 $\mu$amp cm$^{-2}$; Curve 3—0 $\mu$amp cm$^{-2}$. pH was 9.0.
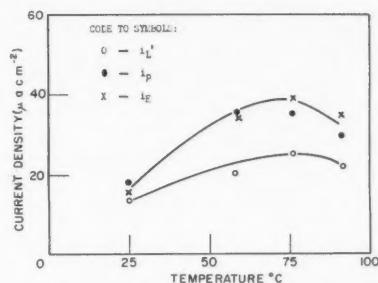


Figure 5—Dependence of $i_L'$, $i_p$, and $i_E$ for iron in a 110 ppm NaCl solution on the temperature. pH ranged from 9.0 to 9.5.



Figure 4—Cathodic polarization curves of iron in a 110 ppm NaCl solution at various temperatures. pH ranged from 9.0 to 9.5.

$$Fe = Fe^{++} + 2e \quad (3) \left.\begin{array}{l} \\ \end{array}\right\} \text{at the anodic areas}$$

According to the film theories of Evans[5] and Müller[6] the anodic areas are pores in a cathodic iron oxide or hydroxide film. The products from the electrochemical reactions and from the reaction,

$$2Fe^{++} + \tfrac{1}{2}O_2 + 2H^+ = 2Fe^{+++} + H_2O \quad (4)$$

react to form insoluble corrosion products or rust.

The rate of corrosion is related to the difference between the polarized potential of the local cathodes ($E_K'$) and the polarized potential of the local anodes ($E_A'$) by Ohm's Law.

$$E_K' - E_A' = i_L (R_S + R_K + R_A) \quad (5)$$

where $i_L$ is the corrosion current, $R_S$ is the solution resistance, $R_K$ is the cathodic film resistance, and $R_A$ is the anodic pore resistance.

The polarized potentials of the local anodes and cathodes may be represented by a sum of potentials,

$$E_K' = E_{K_1} + E_{K_2} + \eta c_1 + \eta c_2 + \eta a_1 + \eta a_2 \quad (6)$$

$$E_A' = E_{A_3} + \eta c_3 \quad (7)$$

$E_{K_1}$, $E_{K_2}$, and $E_{A_3}$ are equilibrium potentials for reactions (1), (2), and (3) respectively. $\eta c_1$, $\eta c_2$, $\eta c_3$ are concentration overpotentials for reactions (1), (2) and (3), respectively. $\eta a_1$ and $\eta a_2$ are activation overpotentials for reaction (1) and (2) respectively. The activation energy for metal dissolution is believed to be small[7] and was not included in the equation for $E_A'$.

The open circuit cathodic current

density ($i_L'$) for iron corroding in 110 ppm NaCl solution with zero applied current is plotted versus the temperature in Figure 5, assuming that the total anodic areas are negligible compared to the total cathodic area of the specimen. This assumption is probably valid if, in fact, the local cathodic area is an oxide film containing pores or discontinuities which act as anodes. $i_L'$ goes through a maximum at about 75 C (Figure 5). Speller[8] has first observed this effect of temperature on the rate of local corrosion of steel in a system open to the atmosphere. He considered the decrease in corrosion rate in the open solution to be due to the decreased solubility of oxygen at higher temperatures since in a closed system he observed no maximum but a steady increase of corrosion rate with increasing temperature.

*Rate Controlling Corrosion Reaction*

The rate controlling corrosion reaction may be determined by considering equations (5), (6), and (7). In the presence of oxygen, the rate of reaction (1) is small compared to the rate of reaction (2) and may be neglected at zero applied currents. The rate of corrosion is given by the equation,

$$i_L = ((E_{K_2} + \eta c_2 + \eta a_2) - (E_{A_3} + \eta c_3)) / (R_S + R_K + R_A) \quad (8)$$

The solution resistance ($R_S$) decreases slightly with temperature. There appears no *a priori* reason to suspect that the protective nature of the corrosion products and, thus, ($R_K + R_A$) is affected greatly by oxygen concentration or temperature in the range studied. The chemical nature of the corrosion products is the same at room temperature and 92 C, as shown by X-ray analysis. Presumably, the polarized potential at the local anodes is not affected by reaction (4), since the steady state concentration of $Fe^{++}$ ions probably is determined by the solubility product of $Fe(OH)_2$ and the pH at the oxygen concentration studied. Thus, it appears that reaction (2), the rate of which is dependent on the temperature and oxy-

gen concentration, is the rate controlling corrosion reaction.

*Application of Cathodic Current*

The application of cathodic current to the iron specimen reduces the corrosion rate until at a value of the current, called the limiting protective current, the corrosion rate for all practical purposes becomes zero (Figures 1 and 2). A qualitative explanation of these curves may be obtained if equation (5) is further consideration.

For cathodically polarized iron a term for the ohmic potential drop due to the applied current must be included in equation (5), which becomes,

$$E_K' - i_a R_K - E_A' = i_L (R_S + R_K + R_A) \quad (9)$$

where $i_a$ is the applied current.

$E_K'$ is a function of the total cathodic current (applied current plus residual corrosion current). $E_K'$ is independent of the applied current for a system which corrodes under complete cathodic control at currents less than the protective value since for this case the total cathodic current remains constant. For currents greater than the protective value and mixed or anodic control, $E_K'$ becomes less cathodic with increasing applied current. With decreasing $i_L$, $E_A' \to E_A$[9, 10, 11] where $E_A$ is the open circuit potential of the anode.

Potential-time curves on cathodically polarized iron indicate that a protective film is formed during cathodic protection. This point will be discussed later. Thus, ($R_K + R_A$) probably increases with the applied cathodic current. $R_S$ would be little affected by the applied cathodic current.

Complete cathodic protection is attained when[12]

$$E_K' - i_a R_K = E_A \quad (10)$$

The protective current ($i_p$) obtained from the weight loss data for iron in 110 ppm NaCl solution is plotted versus the temperature in Figure 5. The fact that cathodic protection is attained with a current not greatly in excess of $i_L'$ at room temperature indicates that for this

case the iron corrodes under cathodic control. A mixed cathodic-anodic control probably occurs at the higher temperatures since a significant change in the total area of the cathodes seems unlikely. A maximum occurs in the protective current versus temperature curve as would be expected.

The general shape of the polarization curves for iron in 110 ppm NaCl solution (Figure 4) are similar to the cathodic polarization curves obtained by Evans, Bannister, and Britton[13] for iron in room temperature experiments. They did not observe the unsteady potentials in the region BC of the polarization curve. BC represents depolarization by oxygen and the branch CD represents evolution of hydrogen. Britton et al considered that the corner point B, which was clearly defined in their polarization curve, represents the protective current density. They verified this for steel by experiments using ferricyanide as indicator. Later workers[14, 15] have shown that determination of the protective current in this manner from polarization curves may lead to low values of the protective current as compared to direct methods.

### Potential Break Method

Mears and Brown[9, 10] have shown, theoretically, that the potential break method is valid only for a system which corrodes under complete cathodic control and that low results would be expected for cases of corrosion under mixed or anodic control.

It is not possible to apply the potential break method of determining the limiting protective current to the results obtained in this work, since in this region of the polarization curves the observed potentials are very unsteady (Figures 3 and 4). However, an empirical criterion may be used to determine the protective current from these polarization curves over the temperature range studied. The criterion is: the protective current is the current density ($i_E$) required to polarize the iron to a value, not necessarily a steady value, of —0.5 volt on the hydrogen scale. It can be seen from Figure 5 that satisfactory agreement between $i_P$ and $i_B$ is attained for cathodically polarized iron in 110 ppm NaCl solution.

Potential-time curves observed by Britton et al[13] on cathodically polarized iron indicate that a protective film is formed during cathodic protection. Curve 3 in Figure 3 was obtained on reducing the current from 10 μ amp. cm.$^{-2}$ to zero current. The observed slow drop of the potential to a less cathodic steady potential indicates, in agreement with Britton et al, that a protective film had been formed at 10 μ amp. cm$^{-2}$ which breaks down in the absence of the applied cathodic current.

No plausible explanation for the unsteady potentials which were observed at applied currents in the region of the protective current (BC in Figure 4) can be suggested. Mellors and Cohen[16] have observed a similar effect for iron in chloride solutions containing various concentrations of the inhibitors NaNO$_2$, and Na$_3$PO$_4$. These workers observed very unsteady potentials for iron with concentration of the inhibitor in the region of near protection; steady active and passive potentials were observed at lower and higher concentrations of the inhibitors, respectively.

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# Corrosion Rates of Mild Steel In NH₄NO₃-NH₃-H₂O Solutions*

By NORMAN HACKERMAN,* RAY M. HURD* and EARL S. SNAVELY*

## Introduction

AMMONIATING LIQUIDS are used extensively both as a spray-applied fertilizer and as a source of nitrogen in mixed fertilizers. These solutions contain anhydrous ammonia, ammonium nitrate, and water in varying ratios, with a total nitrogen content of about 40 to 50 percent by weight. The physical properties of these solutions, including solubility relationships, are summarized in a recent publication.[1] The high nitrogen content, liquid form, and relatively low vapor pressure make these solutions attractive through ease of handling and transportation. Another advantage is the ease with which other plant nutrients, phosphates and potash, may be incorporated to form the so-called "complete mix" liquid fertilizers.[2]

A major problem in the use of these liquid fertilizers is their corrosive nature toward common materials of construction. Severe corrosion has been encountered in steel tanks and equipment used for transporting and storing uninhibited solutions.[3,4] Various sulfur and arsenic-containing compounds, such as thiocyanates, arsenites, thiourea, and mercaptols, have been investigated as possible inhibitors for the ammoniating liquids.[5,6]

The object of the present investigation was to get rates and characteristics of the corrosion reaction, and to determine the effectiveness of ammonium thiocyanate as an inhibitor under conditions likely to be encountered in the use of these solutions.

## Experimental

The nitrogen solutions were prepared from prilled fertilizer grade ammonium nitrate, tap water, and anhydrous ammonia in the proportion 4:1:1 by weight, respectively. The pH of the solutions at 25 C was 10.9 ± 0.1. The validity of results obtained by the use of this grade of ammonium nitrate was checked by several runs with reagent grade chemicals and distilled water. The results were in complete agreement.

All steel coupons were cut from the same sheet of cold-rolled SAE 1020 mild steel. They were annealed at 800 C in a helium atmosphere, smoothed with emery paper, pickled in dilute hydrochloric acid, and washed with water. The procedure for stressed coupons was the same except that the steel was heated to cherry-red and quenched in water before pickling with hydrochloric acid.

The corrosion runs were made in 4-ounce glass bottles containing about

## Abstract

Corrosion rates of mild steel in mixtures of NH₄NO₃-NH₃-H₂O were measured at temperatures of 30, 45 and 60 C. The effects of various sulfur and arsenic-containing inhibitors were studied, with particular emphasis on NH₄CNS. The corrosion reaction was found to be markedly affected by stresses in the metal to the extent that completely stress-relieved coupons would not corrode at all. The rate of the uninhibited reaction was much lower at 45 and 60 C than at 30 C, indicating a change in the mechanism of the corrosion reaction.

The uninhibited corrosion rate of 3700 mdd at 30 C was decreased to approximately 25 mdd with NH₄CNS concentrations greater than 0.1 percent. At 45 C, the most effective inhibitor was found to be 0.05 percent 2-mercaptoethanol + 0.05 percent sodium arsenite, followed closely by 0.1 percent NH₄CNS + 0.05 percent sodium arsenite. Thiocyanate and thiourea alone at concentrations of 0.1 percent were somewhat less effective.

Simple potential measurements using a platinum reference electrode showed the corroding coupons to be about 0.9 volt more anodic than the stress-relieved coupons.              4.3.4

200 cc of the nitrogen solution and sealed by means of a bakelite screw cap with a polyvinyl gasket. Only one 1 inch x 1½ inch x 1/16 inch coupon was placed in each bottle so that the ratio of solution volume to apparent metal surface area was about one liter per square decimeter. The coupons were supported on glass rods approximately in the center of the bottle and out of reach of the voluminous pale to dark green corrosion products which subsequently accumulated in the bottom of the jar (see Figure 1).

Most of the corrosion rates were determined by preparing three or four identical jars which were opened periodically for removal of the coupons, which were then cleaned, weighed and replaced for another period of time. This process was repeated until the character of the plot of weight loss versus time was firmly established.

In actual service the protective nature of the corrosion products must be considered, so another method was used in which a separate coupon was weighed for each point on the weight loss—time curve. This method, which required an excessively large number of coupons for each run, was used only until it had been established that substantially identical corrosion rates were obtained by each method.

Runs were made at 30, 45, and 60 C by submerging the jars in a water bath which was thermostated at the desired temperature. At 60 C it was necessary to seal the jars in a length of 2¼-inch pipe closed with caps to prevent loss of ammonia (see Figure 2). In order to minimize loss of ammonia, these miniature autoclaves were cooled under the

tap before opening for examination of the coupon. Provision was made for pressurizing the autoclaves in order to study the effect of air on the corrosion rate.

The corrosion product adhering to coupons in the uninhibited solutions was a pale green gelatinous precipitate which turned dark green on exposure to air. This coating was easily washed away with water, leaving a very bright metallic surface on the coupon. When thiocyanate or thiourea was used as an inhibitor, a dark-brown to black corrosion product was observed, which also could be easily washed away, leaving a smooth, gray surface on the coupon. No pitting type corrosion was observed in any of the tests.

## Results

### Effect of Stress

While it was found that the uninhibited nitrogen solutions were very corrosive under the conditions used, it was observed that stress-relieved coupons were not attacked at all, even at temperatures as high as 60 C. A large number of the stress-relieved coupons were placed in solutions, both uninhibited and containing various amounts of ammonium thiocyanate, for a period of over three months at 30 C. The coupons maintained their original bright surface throughout the entire period, and showed no weight loss whatsoever. The temperature of these experiments was then raised to 45 C for one week, and then to 60 C for another week, but still no attack took place.

Coupons in which stresses were present corroded at the extremely rapid rate
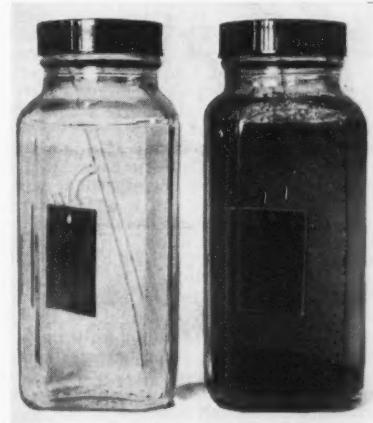


Figure 1—Corrosion test bottles at the beginning of an experiment (left) and after three days with uninhibited fertilizer solution at 30 C (right).

Figure 2—Pressure equipment for runs at 60 C.

**TABLE 1—Corrosion Rates in Ammoniating Liquids***

| Inhibitor | TEMPERATURE | | |
|---|---|---|---|
| | 30C | 45C | 60C |
| None................. | 3700 | 1050 | 1080 |
| 0.01% NH₄CNS...... | 3200 | .... | .... |
| 0.04% NH₄CNS...... | 58 | .... | .... |
| 0.07% NH₄CNS...... | 40 | .... | .... |
| 0.10% NH₄CNS...... | 24 | 170 | 850 |
| 0.40% NH₄CNS...... | 20 | .... | .... |
| 0.70% NH₄CNS...... | 34 | .... | .... |
| 1.0 % NH₄CNS...... | 18 | 140 | 200 |
| 1.5 % NH₄CNS...... | 22 | .... | .... |
| 0.1 % NH₄CNS + 0.05% Sodium Arsenite............ | 9 | 25 | .... |
| 0.1 % Thiourea...... | .... | 120 | .... |
| 0.05% Mercapto-ethanol + 0.05% Sodium Arsenite............ | .... | 3.5 | .... |

* Milligrams per square decimeter per day.
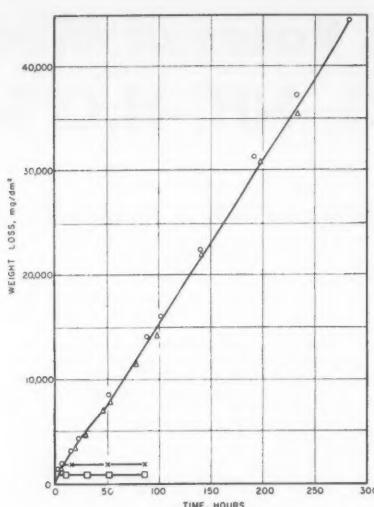


Figure 3—Weight losses in uninhibited solutions at 30 C. Runs in which the coupon stopped corroding abruptly are indicated by X's and squares; runs in which the coupon was completely destroyed are indicated by circles and triangles.
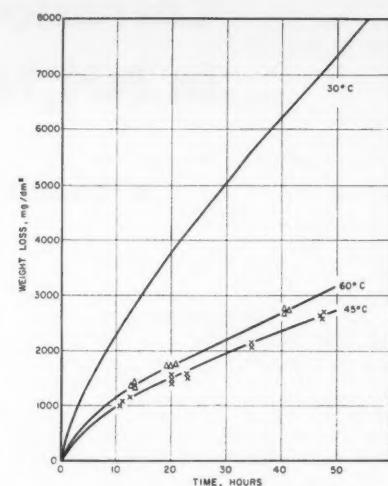


Figure 4—A comparison of weight losses in uninhibited solutions at 30, 45 and 60 C.



Figure 5—Weight losses for three runs in fertilizer solutions containing 0.1 percent NH₄CNS at 30. C.

shown in Figure 3. Occasionally one of the stressed coupons would stop corroding abruptly after the loss of only a fraction of its initial weight. This effect is illustrated by the horizontal portion of the curves of Figure 3. Generally the coupons corroded until they were completely dissolved. The cause for the abrupt halt in corrosion is not yet known; however, annealed coupons which were stressed by twisting or bending invariably stopped after only a few hours, indicating that in these cases stresses were present only in the surface.

A few simple potential measurements were made using a high impedance vacuum tube voltmeter and a coiled platinum wire as an inert reference electrode. The reaction on the platinum surface was not known, so the measured potential values could not be correlated with the table of standard electrode potentials. The rapidly corroding coupons had a potential of 0.8 to 1.0 volt anodic with respect to the reference electrode, while the annealed coupons varied between 0.002 and 0.030 volt anodic to the reference. The small potential differences between the platinum and the annealed steel, plus the earlier observation that the annealed coupons are not attacked at all, indicate that stress relieved steel

in these solutions behaves very nearly as an inert electrode itself. The corroding (stressed) coupons in solutions containing 0.1 percent NH₄CNS had a potential of about 1.25 volts anodic to the reference.

Although these potential measurements were not carried out with sufficient accuracy to justify quantitative interpretations, it is apparent that the effect of stress on potential is unusually large. As a first opinion, NH₄CNS seems to inhibit by controlling the cathodic reaction, since the potential is even more anodic in the presence of the inhibitor.

It should be emphasized that it is not *necessary* to heat and quench the steel samples to get the high corrosion rates of Figure 3. The same rates were obtained on samples cut from cold-rolled sheet, with no further treatment, and on short pieces of drawn tubing. For a

short length of drawn tubing welded into a plate, the weld joint corrodes no faster than the parts away from the joint.

### Effect of Temperature

The corrosion reaction of uninhibited solutions changes mechanism completely at some temperature between 30 and 45 C. The corrosion rates at 45 C and 60 C are approximately ¼ of that at 30 C, as shown in Figure 4. Moreover, at the higher temperatures there was no accumulation of the heavy pale-green precipitate observed at 30 C.

### Effect of Air

The corrosion rates at 45 C were unaffected by subjecting the nitrogen solutions to 15 psig of air in the miniature autoclaves. Rates at 30 and 60 C were not measured in the presence of air.

Figure 6—Average corrosion rate versus inhibitor concentration at 30 C.



Figure 7—Weight losses for three runs in fertilizer solutions containing 1 percent NH₄CNS at 60 C.



Figure 8—Comparison of weight losses in solutions containing various inhibitor types at 45 C.

dium arsenite, and (3) 0.1 percent ammonium thiocyanate + 0.05 percent sodium arsenite. The average weight losses obtained from several runs with each are plotted as a function of time in Figure 8, and the best estimates of the steady rate are given in Table 1.

Thiocyanate and thiourea are similar with respect to effects on corrosion rate and appearance of accumulated corrosion products in the nitrogen solution. These solutions yielded a reddish-brown precipitate while those containing the mixtures with arsenite remained essentially colorless.

## Conclusions

The ammoniating solution tested is sufficiently corrosive under normal conditions that mild steel is inadequate for its transportation and storage unless the solution is inhibited.

The uninhibited corrosion rate is much lower at 45 and 60 C than at 30 C, suggesting a change in reaction mechanism.

Stresses play an important part in the corrosion process; however, the manner in which stresses are introduced in the metal does not affect the corrosion rate as cold-rolled steel corrodes at the same rate as quenched steel. Mild steel in which stresses have been removed by annealing remain bright and apparently corrosion free for months in the ammoniating solution.

Sulfur containing compounds of the thiocyanate and thiourea type are effective inhibitors at 30 C but their effectiveness is increased by the addition of arsenites.

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### Effect of Ammonium Thiocyanate Addition

Corrosion rates were measured for nitrogen solutions containing ammonium thiocyanate in concentrations ranging from 0 to 1.5 percent by weight. In most cases the initial corrosion rate was high but after an hour or two the much lower rate shown in Figure 5 prevailed. The steady corrosion rates for the concentrations studied are given in Table 1 and are plotted as a function of thiocyanate concentration in Figure 6. For thiocyanate concentrations above 0.1 percent, the corrosion rate is reduced to about 1/200 of the uninhibited rate.

Thiocyanate is less effective as an inhibitor at higher temperatures (see data in Table 1). While 0.1 percent affords adequate protection at 30 C, higher concentrations are necessary at 60 C. If protection is desired at temperatures up to 60 C, a minimum of 1 percent thiocyanate is needed.

Corrosion rate data at 45 and 60 C for solutions containing thiocyanate were scattered. This is illustrated by Figure 7 which shows data taken on three solutions containing 1 percent thiocyanate at 60 C.

### Effect of Partial Immersion

Runs were made with coupons partially immersed in both inhibited and uninhibited solutions. No localization of attack or increased rate of corrosion was observed.

### Comparison with Other Inhibitors

Since 0.1 percent thiocyanate is a very effective inhibitor at 30 C but somewhat less effective at higher temperatures, comparison with other inhibitors was made at 45 C.

The following inhibitors and combinations of inhibitors were tested: (1) 0.1 percent thiourea, (2) 0.05 percent 2-mercaptoethanol + 0.05 percent so-

# Corrosion of Concrete by Autotrophes*

By J. H. RIGDON[1] and C. W. BEARDSLEY[2]

## Introduction

AUTOTROPHES BELONG to that class of ubiquitous one-celled organisms that are known as bacteria. They are widely distributed in soil and water. The chemistry of the autotrophes is unusual in that while most microbes derive their energy from the oxidation of carbon, autotrophes obtain the energy for their life processes from the oxidation of some other element such as nitrogen, sulfur, or iron.

There is a sulfur cycle in nature just as there are nitrogen and carbon cycles. Many species of saprophytic bacteria are able to reduce the sulfates which are present in natural waters and convert them to hydrogen sulfide. Sulfur autotrophes take the reduced sulfur and oxidize it back to sulfuric acid, and thus they complete the cycle.

Sulfur bacteria are likely to be found wherever warmth, moisture and reduced compounds of sulfur are present. They are present in soil and in natural springs, and they occur in great numbers in sewers. Sewers provide an especially favorable habitat for their proliferation.

The problem of bacterial corrosion of concrete sewers is a serious one which is encountered mainly in warm climates such as prevail in California, Australia, and South Africa. In places where water temperatures in underground conduits remain below 70 F in summer, corrosion of concrete by bacteria is generally not troublesome.

In sewers of small diameter the problem of acid corrosion can be avoided by using clay pipe conduits. This solution is not available for large trunk lines inasmuch as a clay pipe of a diameter greater than 42 inches is too heavy to keep its shape during drying and burning. It has been found that concrete is the most practical construction material for large trunk sewers.

Corrosion of concrete structures does not occur until the sulfur autotrophes become established on the surface. Certain necessary conditions must precede this development. Sufficient moisture must be present to prevent the desiccation of the bacteria. There must be adequate supplies of hydrogen sulfide, carbon dioxide, nitrogen compounds, and oxygen. In addition, soluble compounds of phosphorus, iron and other trace elements must be present in the moisture film. Sewers in the southern part of the United States generally provide all of the conditions necessary for the proliferation of sulfur bacteria.

## Types of Sulfur Bacteria Present

Two morphological types of sulfur bacteria are commonly found in sewers. One is a thread-forming or filamentous type. Under the microscope these look like fungi, and they are, perhaps, more closely related to the fungi than to the true bacteria. On the surface of the black slime that frequently covers sewer walls a gray or white film often may be seen. This film is composed of filamentous sulfur bacteria. The light color is due to granules of free sulfur that are stored in the cells as a reserve energy supply.

There are also non thread-forming sulfur bacteria of four different genera and some twenty or more species. The genus *Thiobacillus* is the one which is most destructive to concrete. It may be distinguished from the others by its failure to accumulate free sulfur in its cells. This genus is remarkable for its tolerance of acid. Sulfuric acid does not completely inhibit the activity of the *Thiobacilli* even in concentrations as great as 5 percent.

Under a microscope, autotrophes of the genus *Thiobacillus* are seen as minute rods with square ends. They measure somewhat less than 1/10,000 inch in length and 1/50,000 inch in diameter. Their small size is offset by their great numbers. In a typical pound of corroded concrete there is likely to be more than two thousand million of these bacteria.

Bacteria of the genus *Thiobacillus* do not consume hydrogen sulfide directly when they are cultured in the laboratory. They appear to prefer free sulfur and polysulfides as substrates. In sewers, hydrogen sulfide is transformed into free sulfur and polysulfides for their use, partly by other organisms and partly by non-biological agencies.

A newly made concrete structure begins its service life in a strongly alkaline condition with free moisture condensed upon its surface having in many cases a pH of about 12. No species of sulfur bacteria will tolerate so alkaline an environment. Therefore the concrete is temporarily free from corrosion.

With the passage of time the free lime of the hardened cement paste is slowly transformed into carbonate by reaction with the carbon dioxide of the air. This neutralization reaction continues until the pH of the concrete has fallen below 9. At this level of alkalinity a species of sulfur bacteria known as *Thiobacillus thioparus* can live. Using hydrogen sulfide as a substrate, these organisms generate thiosulfuric and polythionic acids. The pH of the surface moisture steadily declines and the concrete becomes host to other organisms which are concerned with the oxidation of sulfur.

When the surface moisture has become distinctly acid the autotrophes of the species *Thiobacillus thioxidans* and

## Abstract

The various types of sulfur bacteria which can be present in concrete sewers are described and conditions which are necessary for their existence are listed. There are three steps in the destruction of concrete sewers by autotrophes: (1) production of hydrogen sulfide by the reduction of sulfates or by the action of proteolytic bacteria, (2) oxidation of the hydrogen sulfide to sulfuric acid by the sulfur bacteria, and (3) decomposition of the calcium silicates of the portland cement by the sulfuric acid. A number of countermeasures which can be taken to prevent these conditions are discussed. They include the designing of sewers for rapid flow, ventilation, and the use of protective coatings.                            3.3.4

the closely related species *Thiobacillus concretivorus* begin to proliferate. These organisms do not thrive on neutral or faintly acid surfaces. But below a pH of 5 they become active and begin to generate sulfuric acid. The habitat becomes too acid for competing species to survive. The concrete softens to a plastic consistency while the pH of the free moisture declines to a level of 2 or less.

Although in most environments concrete is remarkably stable and durable, the calcium silicates and aluminates that compose the cement are reactive. They are decomposed by acids and by solutions of certain salts. Cement bonded products such as concrete, mortar and transite are slowly disintegrated by weak organic acids. The attack of strong mineral acids is much more rapid. No cement bonded product can long withstand the action of sulfuric acid.

## Corrosion Process

A corrosion process can usually be analyzed into a sequence of steps. When this is done the process may be halted by interrupting the sequence at any one of the steps. There are four steps in the destruction of concrete sewers by autotrophes: (1) Production of hydrogen sulfide in the sewage by the reduction of sulfates and the decomposition of proteins. (2) Escape of the hydrogen sulfide from the sewage into the sewer atmosphere. (3) Oxidation of hydrogen sulfide to sulfuric acid by sulfur bacteria. (4) Decomposition of hardened cement pastes by sulfuric acid.

Interrupting this sequence at any step will save the concrete. Corrosion prevention has been attempted by various methods which seek to obstruct one or more of these steps.

Prevention of the build-up of hydrogen sulfide in sewage has been attempted with some success by designing sewers for rapid flow. Increased turbulence in the flowing stream promotes oxygen absorption at the surface. When absorbed into the water, oxygen tends to prevent the reduction of sulfates and to destroy hydrogen sulfide already present.

Several formulas have been developed to enable the engineer to determine velocities which will prevent sulfide build-up. When using them it should be realized, however, that the activities of complex biological systems cannot be reliably predicted by mathematical formulations. Obscure determinants which cannot be taken into account may intervene to produce unexpected results. A forecast as to whether generation of sulfide will take place in a projected sewer line can never be more than an estimate of probabilities.

The build-up of hydrogen sulfide in sewage may be retarded or prevented by cleaning the sewer and especially by removing sludge deposits from the bottom and slime growths from the walls. The effectiveness of such measures is only temporary. In warm weather slime growths form again in about thirty days. In lines where flow velocities are low, sludge deposits accumulate in a few months.

### Chemical Treatments

There are several different chemical treatments that may be used to suppress the first step of the corrosion sequence. Chlorine or hypochlorites of sodium or calcium may be added to the sewage. These oxidants have a strong bactericidal action which reduces the numbers and activity of the organisms that generate hydrogen sulfide. Sulfides that are already present are oxidized to sulfate.

Treatment of the sewage with sodium nitrate reduces the production of hydrogen sulfide. The nitrate acts as a source of oxygen to the bacteria and no sulfate is reduced to sulfides as long as nitrate is present. The addition of about 30 ppm of nitrate to sewage has been found to delay the formation of sulfide for about 24 hours.

Other chemical treatments are available. Chemical treatments find little practical application, however, for they are generally too expensive for regular use on large volumes of sewage. Occasionally they are useful for specific small scale applications. When the required reagents may be obtained from available industrial wastes they are especially advantageous.

### Escape of Hydrogen Sulfide

The second step of the corrosion sequence is the escape of hydrogen sulfide from the surface of the sewage into the sewer atmosphere. The tendency to escape may be decreased by increasing the pH of the sewage. Increasing alkalinity causes unionized hydrogen sulfide to pass over into the ionized condition, and it is only the unionized sulfide that is able to escape as a gas from the surface of the flowing stream. Hydrated lime is the cheapest and most economical chemical for this type of treatment.

Various other chemical treatments are available for inhibiting the second step of the corrosion sequence. Soluble salts of such metals as copper, zinc, and iron may be added to the sewage. The ions of these metals precipitate hydrogen sulfide from solution as insoluble metallic sulfides. As long as they are present no sulfide can escape into the air. Copper is especially effective, for the ions have a strong bacteriostatic action and they effectively inhibit further generation of sulfide by the bacteria.

No hydrogen sulfide escapes from solution when the sewer flows full to the top. This condition prevails in force mains and inverted siphons and thus conduits of this type are never affected by sulfide corrosion. It is not economical to design collecting lines and trunk sewers to run full to the top. Such designs make no provisions for the variations in flow and for the increased capacity which inevitably becomes necessary.

### Oxidation of Hydrogen Sulfide

The third step in the corrosion sequence is the oxidation of hydrogen sulfide to sulfuric acid. This conversion is effected by sulfur autotrophes proliferating on the moist sewer walls above the flowing stream. These organisms require a regular supply of hydrogen sulfide, carbon dioxide, nitrogen compounds and oxygen. They also need a moist surface on which to live. Interruption of this step of the corrosion sequence may sometimes be accomplished by ventilation of the sewer. If a flow of air is maintained through the conduit in sufficient volume to dry out the walls, the sulfur bacteria cannot survive. Ventilation also is an effective method of reducing odor nuisances which are likely to result from the same conditions that lead to acid corrosion by autotrophes. Where ventilation can be practised it is an effective way of dealing with corrosion and odor problems.

Ventilation of sewers is generally not practical in densely populated districts unless the air which is withdrawn from the sewer is deodorized. The volumes of air which must be handled to secure effective odor and corrosion control range from 10,000 to 50,000 cubic feet per minute. Deodorization of sewer air in such quantities presents serious engineering problems which may have no economically feasible solutions.

Another method of inhibiting the conversion of sulfide to sulfuric acid often occurs to engineers when they study the corrosion of concrete by autotrophes for the first time. It has the appearance of a simple, easy, and economical solution to the problem. The sewer wall may be coated with a bactericide which will prevent the autotrophes from growing.

An extensive series of experiments of this type was carried out by one of the authors in the San Fernando Valley outfall sewer in 1953. Areas of the sewer wall were carefully cleaned and coated with every type of disinfectant and bactericide and fungicide that seemed cheap enough to be practical for large-scale use. Such compounds as copper naphthenate, rosinamine acetate, pentachlorophenol, orthodichlorobenzene, trichlorobenzene, and various quaternary ammonium compounds were tested. None of these compounds were effective for more than a few weeks.

If the compound was soluble in water the effect lasted only a few days. If it was completely insoluble it did not inhibit the bacteria. If, like pentachlorophenol, it was very slightly soluble the bacteria would be held back for a few weeks. Then they would slowly extend their slimy films over it and start proliferating in the usual way.

### Disintegration of Concrete

The fourth step in the corrosion sequence is the disintegration of the concrete by the acid which the autotrophes have produced. Various expedients have been tested for counteracting the attack at this step.

Acidproofing admixtures which may be incorporated into the concrete at the time that it is made are sometimes advocated. The claims for these products can seldom be verified. Water-repellent substances, when used in a dense well-graded concrete mix, may serve to slow the rate of attack. Mere slowing-down of the attack does not constitute acid-proofing. It has never been shown that any admixture or compound which is incorporated into the concrete at the time of mixing, will make it immune to strong acid. A concrete mix is necessarily made with water and it remains permeable to water and to acids in water solution after hardening. Hardened cement pastes are soluble in strong acids and it is unlikely that immunity to acid attack can be built into any product that is bonded with portland cement.

The character of the aggregate has only a minor effect on acid resistance. A coarse aggregate may contribute mechanical protection when water velocities are high. The corrosion product of the cement mortar which bonds the aggregate together, is a semi-gelatinous paste of sand and gypsum. When the coarse aggregate has been partially exposed the projecting surfaces of the larger pieces help to hold the sand-gypsum paste and keep it from being swept away. The paste thus remains to interpose a barrier between newly formed acid and the unreacted cement. When it has accumulated to a depth of an inch or more further corrosion becomes very slow. The coarse aggregate, after exposure, may thus contribute to the protection of the concrete.

### Use of Protective Coatings

Another method of inhibiting the acid corrosion is a familiar one to corrosion engineers. The concrete may be given a protective coating. Three factors affect the ability of the coating to protect the concrete: (1) Chemical resistance of the coating to acid. (2) Impermeability of the film. (3) Adhesion of the film to the concrete. The coating must have these properties in full measure and retain them unimpaired over a long period if it is to be successful.

Many organic coatings are resistant to acid. The copolymers of butadiene and styrene, the vinyl chloride copolymers, and the bisphenol epichlorhydrin polymers, all have excellent acid resistance. Bituminous materials, such as asphalt and coal tar also have this property.

Surface coatings of such materials are effective in the degree that they keep the acid away from the concrete. Adequate protection depends upon long continued impermeability. Coatings that are brushed, sprayed, or rolled on seldom give complete protection. Such coatings are likely to have minute perforations or pinholes that permit the acid to pass through. When this happens the imperfections rapidly increase in size, until the entire surface is involved. Relatively good protection or almost complete protection is not good enough.

Consider the case of an organic coating on concrete. The protecting film is inert to acid and almost completely continuous. The continuity of the film is so perfect that there is only minute perforation a few thousandths of an inch in diameter in each square foot of coating. These defects involve only about one part in fifty million of the surface and they cannot readily be detected by visual inspection.

In service in the sewer such defects are fatal. The acid penetrates through the perforation and attacks the concrete behind it. The concrete reacts and expands enlarging the breach in its protecting cover. Disruption spreads from each perforation.

A successful means of protecting concrete sewers from acid attack has been to cover the surfaces exposed to the activity of the autotrophes with sheets of PVC plastic. The forms over which the concrete is cast are lined with the sheets. When the forms are removed the interior surfaces of the conduit are protected by the dense and impermeable plastic. The sheets are about six hundredths of an inch thick. In service they are firmly held in place by T-shaped projections which are integrally molded with the sheet and embedded in the concrete. The joints between the sheets are covered with weld strips. At the completion of construction the continuity and impermeability of the plastic sheet may be verified with a spark tester.

The protection afforded by these plastic sheets anchored in place by T-lock projections has proved satisfactory in service. Installations which were made ten years ago are still in excellent condition. The full term of service of which they are capable is as yet unknown, although the useful life will certainly be much longer than ten years. Gradually a slow stiffening of the plastic occurs. This change may be due to loss of plasticizer or to physical and chemical changes that take place at a very slow rate. The hardening that occurs in the first ten years does not appear to be detrimental.

Another method of protection is a lining of vitrified clay tile. This method has been employed extensively by the City of Los Angeles. The tiles which are generally about 12 x 18 inches, are molded with anchoring lugs at the back. They are laid with their faces against the concrete forms and the concrete is cast over them. When the forms are removed the tiles are held in place by the anchoring lugs.

Several precautions should be observed if concrete is to be protected by tile liners. The joints between the tiles must be sealed with an acid-proof jointing compound and the porosity of the tiles must be kept to a minimum.

Care should be taken to secure concrete aggregates that are stable and non-reactive.

Failure to observe these precautions may lead to the loss of the protecting cover from the concrete. Ceramic clay is a brittle material. Any chemical reaction of the concrete that results in expansion will break the anchoring lugs and allow the tile to drop. Such reactions have occurred by penetration of acid through the joints between the tiles and through capillary chanels in porous tiles. Tiles also have been broken loose by expansive reactions of concrete aggregates with the alkalies of portland cement.

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**Any discussions of this article not published above will appear in the June, 1958 issue**

## ERRATA

**Corrosion Products of Mild Steel in Hydrogen Sulfide Environments** by F. H. Meyer et al. Corrosion, Vol. 14, No. 2, 109t-155t (1958) Feb.

Page 113t, column 1, line 11 should read:

10. Figure 9 shows that the reactions

On page 114t, column 3, lines 8 and 9, statement (2) beginning "more hydrogen ions . . ." should be deleted.

On page 110t, two changes should be made in Table 1. In first line of column 3 the formula for crystal structure type for kansite should read "Co₉S₈" instead of "C₉OS₈". In line 4 of column 7, the magnetic susceptibility of phrrhotite should read "Ferrimagnetic" instead of "Ferromagnetic".

# Success Is Reported With Squeeze Inhibition

## Silicon Iron Anodes Replace Carbon in Cable Duct Run

Substitution of high silicon cast iron anodes for carbon anodes has been proposed as one expedient for temporary protection of a number of lead cables in a tile duct run. Eventually, according to the report made to a T-4B Corrosion of Cable Sheaths Committee meeting at St. Louis during March, 1957, the cables will be replaced with others having non-metallic protective coverings.

This discussion developed during a report in which graphite anodes used in a cable duct carrying between one and 1¼ amperes had developed deposits of products with the appearance of lamp black at intervals of one foot, apparently coinciding with the joints in the duct line. The anodes were not under water for any length of time. Lead sheaths were maintained at a potential of about 0.5 volt negative.

A strong odor of chlorine gas was noted when the sealed ducts were opened.

## *Equipment Variety Unimportant in Dynamic Testing*

Results of dynamic tests of inhibitor efficiency made by nine oil company laboratories show about the same results when inhibition in the 90 percent area is achieved. This is true no matter what kind of variation is used in the type of equipment used in the test, one member of T-1K-1 told a meeting of T-1 at Oklahoma City during the October South Central Region meeting there. When efficiencies in the 50 percent range are compared, however, there is a wide dispersion of results, approximately what would occur in results of one experimenter alone.

This information was given as a result of discussions on the task group's work on a dynamic inhibitor test. The group aims at establishing tests for sour and sweet systems of two types, one for screening and one for evaluation.

One of the aims of the group is to derive correlations related to oil-brine ratio and inhibitor concentration which will eliminate the need for testing every inhibitor in every well before using. The significant factor seems to be the ratio of inhibitor versus the oil, although the concentration must be increased when the water:oil ratio goes up because more inhibitor is leached into the water.

Initial evidence developed by the group indicates that factors such as size of flasks, volume of material used and number of rotations per minute are not critical.

## Electrical Probe Sometimes Gives Erratic Readings

Erratic results have been reported from electrical probe corrosion measuring instruments exposed in oil wells. Members of T-1 discussing the instruments at a committee meeting in Oklahoma City said that these effects apparently resulted from deposits on the electrode from oil well fluids.

One member reported that when the probe became coated, pitting attack occurred at the end where it was insulated and that this corrosion did not register on the dial.

## *Task Group Formed On Chemical Cleaning*

A task group on chemical cleaning has been formed by Unit Committee T-8. Mr. F. B. Hamel, Standard Oil Co. (Ohio) has been appointed to serve as temporary chairman. The task group will serve as a clearing house for reports of both good and bad engineering procedures and results; make specific recommendations as to how chemical cleaning operations can be better controlled and prepare certain recommended procedures for performing the chemical cleaning operations.

**Hamel**

The task group plans to have a preliminary meeting in San Francisco.

## Fritts Elected Head of T-6E Coatings Unit

Unit Committee T-6E, Protective Coatings in Petroleum Production, has elected C. J. Fritts, Socony Paint Products Co., Houston and F. E. Blount, Atlantic Refining Co., Dallas, chairman and vice chairman respectively.

Mr. Fritts has been concerned with corrosion control since 1949. He has a BS in industrial chemistry from the University of Kentucky.

**Fritts**

Mr. Blount has been a member of NACE for five years. He has a BS in chemistry and has had six years' experience in corrosion work in the U. S. Navy.

## *Two Factors Given For Successful Use of Method*

Successful inhibition of corrosion in oil wells using the squeeze method seems to depend on: First, getting a substantial coating of inhibitor on corroding surfaces. Secondly, squeezing inhibitor into the formation so that its gradual return to the well repairs the depleted inhibitor and maintains the film. When these two conditions are met squeeze methods usually produce good results, according to members of T-1. These facts developed during a committee session at the NACE South Central Region conference at Oklahoma City.

Several members reported on squeeze-inhibition experience. One member said 100 wells have been treated successfully, while another said numerous wells over a wide geographical area had been so treated successfully every three months, except that wells making sand get needed treatment every 18 days.

#### Tubing Life Extended

Checks on the efficiency of the squeeze method are made by recording iron content, tubing surveys and from replaced equipment. One report indicated that in one field tubing life before squeeze inhibition started was from 3 to 9 months and that after inhibition tubing was still good after two years.

Another member reported tests on oil and condensate wells with one successful and two questionable. Coupons exposed in the well during inhibition treatment indicated 98 percent protection for the first three weeks. This declined steadily to 35 percent after six months. In this test a long-term series of coupons was exposed before inhibition started and as they were withdrawn for inspection, they were replaced with short term coupons.

The short term coupons indicated no protection after three weeks. This difference in reaction between the long and short term coupons was the basis for the hypothesis on inhibition mechanism involving initial coating with a heavy slug of inhibitor. The volume of inhibitor leached from the formation was unable to protect the new coupons but sufficient to maintain protection on the old ones.

#### Others Results Noted

Of all wells squeezed the method seems to have adversely affected production of only one. The consensus was that there was more improvement than bad effects from the treatment.

Nearly everyone using the squeeze method tests inhibitors in well fluids for compatibility.

It is estimated that 150 wells have been given squeeze inhibition.

## Data From 43 Wells Over 5000 psi Tubing Pressure Encourages Committee's Inquiries

Some data have been received by T-1B-1 High Pressure Well Completion and Corrosion Mitigation Procedure which have encouraged the committee to ask for data from every well with tubing pressure over 5000 psi. The basic information collected is designed to give the committee a basis for considering corrosion mitigation measures.

At a meeting of the committee in Oklahoma City during the South Central Region NACE conference there the committee reported the following data have been received from 12 companies cooperating:

43 wells are described, including two dual wells.

Bottom hole temperature range, 173-300 F.

Bottom hole pressure range, 6220-12,395 psi.

Carbon dioxide content, 0.09—3.30 percent.

Salt water chloride content, 20 to 99,000 ppm.

Iron content of water, 20—480 ppm.

13 operations used stainless steel in some form.

The committee plans to extend its inquiry to cover almost all wells with tubing pressures in this range.

## Bruckner and Compton Head De-Icing Salt Unit



Bruckner　　　　　Compton

Unit Committee T-4D, Corrosion by Deicing Salts has elected W. H. Bruckner, University of Illinois, Urbana and K. G. Compton, Bell Telephone Laboratories, Murray Hill, New Jersey, chairman and vice chairman, respectively.

Mr. Bruckner is a research associate professor of electrical and metallurgical engineering at the University of Illinois and a technical director of the cathodic protection laboratory there. He has been on the research staff of the Naval Research Laboratory, American Smelting and Refining Company and the Crucible Steel Company.

Mr. Compton has worked with corrosion problems for more than 25 years at Bell Telephone Laboratories. He has been active on corrosion committees of several technical societies. He received his training in electrical and chemical engineering and in electrochemistry at the State College of Washington.

## Dump Bailer Method Successful on Over 84 Percent of Wells

Successful inhibition of 84 percent of 746 oil wells by the use of the dump bailer was reported to T-1 at its Oklahoma City meeting last October. Results with the dump bailer were good in all but 5 to 7 cases.

Among the points raised during the discussion were:

1. About 2½ quarts are dumped at 15-day maximum intervals.

2. Four wells treated with the dump bailer technique at 10-day intervals have shown no drop in iron content but caliper surveys indicate no increased corrosion.

3. Large bailers are being made to hold at least 4 quarts.

4. One operator found no difference in results related to inhibitor concentrations of 20, 50 and 80 percent active inhibitor. This operator uses 80 percent active inhibitor.

5. When an inhibitor is pumped into a well it seems to protect the top and middle zones, as indicated by caliper surveys. When started at the bottom, the bottom is protected and then the protection diminishes toward the top of the well.

### Stressed Coupons Used

Some use of stressed coupons in well heads to get data on stress as well as corrosion has been reported to T-1. This is being done in Canada as well as in parts of the United States.

## Wire Line Retrievable Valves Used in East Texas

Wire line retrievable subsurface valves are being used in some East Texas sour crude wells. The valves are being installed in an effort to permit injecting inhibitor into the annulus through the valves.

One member reported that an initial experiment with 38 subsurface valves was satisfactory because only 4 to 5 percent of them worked. The method involves injection of either water or oil soluble inhibitors.

## Plastic Coated Tubing Used

Some wells are being completed with plastic coated tubing and a valving device that permits bringing in without swabbing. Tubing can be unloaded down to 6500 feet using 3000 psi air pressure.

# Coordinating Committee Growth Has Been Rapid

## Fifteen Groups Affiliate With Unit In 2-Year Period

No technical committee organized by the National Association of Corrosion Engineers has acquired in equal time as many affiliates in widely separated places geographically as T-7 Corrosion Coordinating Committee. Credit for this rapid expansion is due principally to the assiduous work of its first two chairmen, J. M. Fouts and C. A. Erickson, Jr. The group is so new that Mr. Erickson still holds the chairmanship.

Authorized by action of the NACE board on March 16, 1956, T-7 has as its principal aim the encouragement of cooperation among committees organized for the protection of underground plant. Since its authorization it has acquired 15 affiliates, in places as widely separated as Toronto, Canada and San Diego, Cal. Members of the committee have been helpful in organizing local committees in several localities, when invited to do so. NACE does not participate in the actual work of the underground corrosion mitigation committees.

### Some Groups Long Active

Some of the committees that are cooperating with T-7 have been operating for 40 years or more, especially those in the older metropolitan areas where electric railways and underground telephone cables were used at the same time. It was one of the aims of the committee that the long experience gained by these older groups could be made available to newer ones, and especially to the new committees that are being formed in many metropolitan areas.

### Problems Grow Pressing

The incentive to organize cooperatively to combat underground corrosion grows more pressing every year. The difficulties encountered in properly engineering the increasing volume of cathodic protection grow as more and more complex structures are placed underground. The economic importance of corrosion damage and pressing considerations of safety—as for example in connection with high pressure gas lines—or property damage, as from a pipe line transporting brine, or chemicals, grows rapidly.

Companies operating these facilities, especially in congested metropolitan areas, frequently find it impossible to protect their structures cathodically except through cooperation with owners of adjacent structures.

### More to Organize

There is no way to tell how many underground corrosion mitigation committees ultimately will be formed, nor how many will affiliate with T-7.

Information coming to NACE about the interest aroused in various parts of the United States, and in at least two instances, from countries in the tropics, shows that many committees will be organized. The advantages of cooperating in the T-7 organization are so great that most of these groups ultimately will choose to work with other similar groups. There are no obvious disadvantages because there is no fee connected with NACE affiliation and NACE exercises no jurisdiction of any kind over the committees.

### Inquiries Are Invited

A subdivision of T-7 has been organized in each of NACE's regions. Local industries concerned with underground corrosion who think cooperative solution of their problems is advantageous may inquire of the chairman of their nearest group for advice and assistance. The names and addresses of these regional officials are published in Corrosion on alternate months beginning with January.

Also listed are the names and addresses of the local committees that have affiliated with T-7. This list makes it possible for an operator of underground plant to learn quickly to whom in which company he must go for data on his corrosion problems or for cooperative efforts in their solution.

## Preparation of Maps Is Principal Activity

Preparation of maps of underground plant and their associated cathodic protection systems is likely to be an important function of local corrosion mitigation committees. The success of the Chicago Committee on Underground Corrosion (L. E. Nichols, Northern Illinois Gas Co., Bellwood, Ill., chairman) in preparing such a map has led to its consideration by other groups.

Houston Corrosion Coordinating Committee is working on a similar map for which members of the committee supply details of their individual systems for posting. This permits easier cooperation of committee members and often points to localities where cooperative mitigation is needed.

## Annual Meeting Is Held At NACE Conference

Among the activities of T-7 is an annual meeting during the National Association of Corrosion Engineers' conference when committee members may discuss their problems and ask for solutions reached by others. Also, if there is sufficient interest, meetings may be held at the regional level for like discussions.

## Pumps Are Not Benefited

The task group on pumps T-1D-2 West Texas-New Mexico reported to T-1 that its initial inquiries show that pumps apparently do not benefit from inhibitors used in oil wells. There is some belief, however, that pumps get about 25 percent protection from inhibitors in well fluids.

## Report to Be Summarized

It is the intention of Task Group T-4B-6 on Stray Current Electrolysis to summarize the interim report on control practices published by the committee in Corrosion's January, 1957 issue. This decision was reached at a meeting of the group at St. Louis in March, 1957.

## Model Organization By-Laws Are Studied

A current project of T-7 Corrosion Coordinating Commitee is the preparation of a set of model by-laws for the information of those seeking to organize local corrosion mitigation groups. These model by-laws will be based on existing by-laws of working organizations and should be of substantial benefit because they will incorporate the tested ideas of old organizations.

The committee also functions to:

1. Receive reports of the activities of local corrosion coordinating groups and publish them when requested.

2. Receive and file matters of procedural interest, i.e., case histories on the solution of underground corrosion mitigation problems. These are available for review by affiliates.

Under advisement also is the expansion and re-issuing of the Report of the Correlating Committee on Cathodic Protection published by NACE in July 1951. This report's recommendations often are used by local committees in solving their cathodic protection problems.

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In addition to those held at the annual national NACE meeting, 36 technical committee meetings were held at regional sessions during 1957.

**ther Wrought Iron case against corrosion**

Photomicrograph T-90-2 (100x) shows a typical area—parallel to rolling—of the microstructure observed in the subject 10-inch wrought iron pipe.
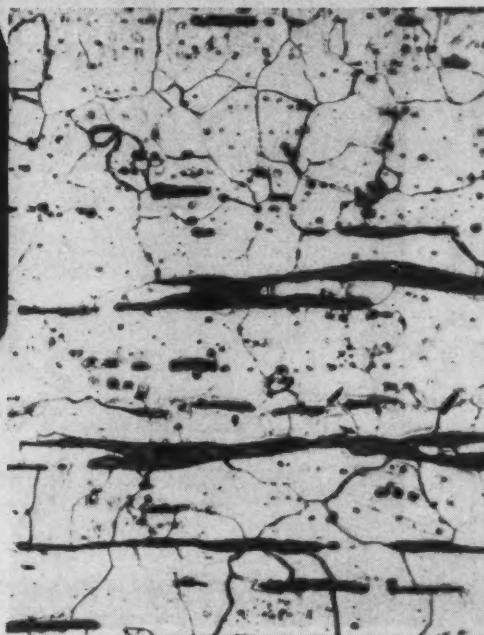
# Metallurgical Report 5460—Fire Protection Line*

This report deals with the metallurgical examination of a length of 10-inch wrought iron pipe, submitted to our laboratory for investigation and comment.

The sample submitted had been in service for over 50 years as a fire protection line, yet proved to be in excellent condition. Both the outer and inner surfaces showed no evidence of localized pitting. No thinning of the pipe wall was observed. The inner surface was covered with a uniform layer of rust tightly adherent to the metal.

## ROCKWELL HARDNESS

A cross-sectional ring was prepared for hardness determination. Hardness values taken around the cross-sectional ring indicated a B66 hardness, typical for wrought iron pipe, and showed that the strength and ductility were likewise normal.

## CHEMICAL ANALYSIS

Carbon—.018%; Manganese—.036%; Phosphorous —.130%; Sulphur—.016%; Silicon—.150%; Iron Silicate—3.59%.

## SUMMARY

Results of the laboratory examination serve as positive identification of the subject sample as wrought iron. Significant is the fact that this sample has successfully withstood corrosive attack for more than fifty years. This is the kind of documentary evidence which has earned wrought iron such an outstanding reputation in corrosion control. A. M. Byers Company, Clark Building, Pittsburgh 22, Pa.

* Name of actual installation given on request.

Write for free cloth-bound book, *Wrought Iron: Its Manufacture, Characteristics and Applications.*

# BYERS
## WROUGHT IRON

# Over 200 Attend Canadian Region's Meeting

PERMIAN BASIN SECTION's technical speaker (right) Charles E. Perry, Sivalls Tanks, Inc., Odessa, discusses his February 10 talk with Jack Collins, Continental Oil Co., left and John V. Gannon, The Texas Company, section chairman and trustee. Mr. Perry talked on "Field Experience in the Protection of Lease Surface Equipment" before 40 members and 23 guests at Odessa.

## Eighteen Technical Papers Presented At Toronto Session

Eighteen technical papers were presented at the three-day meeting of Canadian Region March 3-4. They ranged in topic from corrosion problems in atomic reactors, through cathodic protection and the use of reinforced epoxy resins. The meeting was held at the King Edward Sheraton Hotel. Meeting jointly with Canadian Region was the Associate Committee on Corrosion Research and Prevention, an affiliate of the Canadian National Research Council.

More than 200 persons attended the technical sessions and social events.

H. A. Webster, Corrosion Service Ltd., was chairman of the program committee; A. H. Carr, Koppers Inc., of the arrangements committee and F. Farrer, Trans-Northern Pipeline Co., finance. For the Associate Committee on Corrosion Research and Prevention: H. D. Smith, Nova Scotia Research Foundation, chairman; P. J. Beaulieu, National Research Council, secretary.

The technical papers presented were:

Corrosion Problems in a Reactor, F. H. Krenz, Research Metallurgy Branch, Atomic Energy of Canada, Ltd., Chalk River, Ont.

Corrosion Studies With Steel Welds, H. H. Yates, McGill University, Montreal.

Oxidation of Iron Below 450 C, Morris Cohen, National Research Council.

Cathodic Behavior of Metals, F. E. W. Wetmore, University of Toronto.

Oxidation of Aluminum at Room Temperature, P. M. Aziz, Aluminium Laboratories, Ltd., Kingston, Ont.

Economics of Underground Corrosion Control in the Union Gas Company of Canada, Ltd., Ralph E. Kuster.

Inhibitors Combat Refinery Corrosion, B. Hambley, Alchem, Ltd.

Trans-Canada Pipe Line Corrosion Control Program, Lance Heverly.

A New Technique in Applied Radiography, M. R. Pauschenwein, Canadian Oil Co. Ltd., Corunna, Ont.

Protective Linings for Chemical Plant, W. W. Walker, Dunlop Co.

Electrical Insulation of Underground Pipelines, George B. McComb.

Application of Glass Fiber Reinforced Polyester Plastics as an Engineering Material of Construction in Chemical Environments, Walter A. Szymanski, Hooker Electrochemical Co., Niagara Falls, N. Y.

Reminiscences of a Corrosion Engineer, F. L. LaQue, The International Nickel Co., Inc., New York.

Corrosion Problems in the Petroleum Refining Industry, J. F. Mason, Jr., The International Nickel Co., Inc.

Non-Destructive Testing, R. W. Roberts, Sperry and Budd Nuclear Systems Divisions (Canada) Ltd.

## Pipe Reconditioning Economics Covered at Southwestern Ohio's Meeting on January 28

"Developments in Cathodic Protection," is the topic scheduled for discussion by Marshall E. Parker, Houston consulting engineer at the April 29 meeting of Southwestern Ohio Section at Dayton. The Duriron Company will sponsor the session.

Ralph Madison, Truscon Steel Corp. was the scheduled principal speaker at March 25 meeting at Cincinnati; Roots-Connersville Blower Division of Dresser Industries plant was toured during the afternoon of February 25 and a dinner meeting was held with Elwood B. Norris, Metcutt Research, Inc., discussing "Evaluation of Coatings for Protection of Steel at Elevated Temperatures."

The January 28 meeting at Cincinnati was attended by 21 members and nine guests. Business included appointment of John J. Halbig as section representative at the San Francisco Conference, a report on progress on the October 15-17 North Central Region meeting and appointment of S. C. Jones, Cincinnati Gas & Electric Co., as chairman of a committee to nominate 1958-59 officers.

George Pemberton, Cincinnati Gas and Electric Co. discussed "Evaluating the Economy of Reconditioning and Coating Underground Steel Pipe." This talk, based on experience of his company, considered the economics of repairing corroded pipe versus replacement. Emphasizing that experience is required to make a decision on this question, he said his company has developed a chart from time studies to aid in making the decision.

### Conference Review Coming in May

A review of the events at the NACE 14th Annual Conference and Exhibition at San Francisco will be published in the May issue of CORROSION. Persons who were unable to attend the meeting will be able to get some idea of the conference from this report.

Members of Central Office staff attending contribute to gathering the report. Wide photographic coverage is expected.

Procedure involves cleaning and filling with weld metal and then priming with a wax base material. A special wax coat is then applied and a polyvinylchloride film tape wrapped on. This sequence was demonstrated with the help of S. C. Jones and R. L. Wood.

Considering the cost of new pipe installed at $10 a foot, Mr. Pemberton said, it was economical to repair existing pipe up to a repaired cost of $8.50 a foot. Costs greater than this make the pipe unsalvageable. On a time basis, 10 minutes per foot of welding time is the break-even point between repair and scrap.

Experience shows that average repair time is 5 minutes a foot at a cost of $7.10 per foot for 16-inch diameter pipe.

## Barker Talks on Coatings

During the February 3 Philadelphia Section meeting at the Poor Richard Club guests and members heard J. L. Barker, Carbide and Carbon Chemical Company speak on "Applied Protective Coatings."

## Greater St. Louis Section Hears Educational Talks

The fourth and fifth lectures in a series "NACE Education Course—Corrosion" were presented at meetings of Greater St. Louis Section February 10 and March 10. The fourth lecture "Cathodic Protection Principles for Mitigation of Corrosion on a Natural Gas Distribution System," was presented by Mssrs. V. L. Rasmussen and J. C. Vogt, respectively superintendent and assistant superintendent of Laclede Gas Company's inspection and controls division. A discussion period followed the presentation.

E. G. Holmberg, International Nickel Co., Inc., Detroit was the scheduled speaker for the fifth lecture in the series on "Dynamic and Embrittlement Corrosion."

## Murdison, Parker Named to NACE Policy Committee

Andrew R. Murdison, Pipe Line Division, Imperial Oil Ltd., Toronto, Canada and Ivy M. Parker, Plantation Pipe Line Co., Atlanta, Ga., have been named to the NACE Policy and Planning Committee effective in March.

Mr. Murdison has been active in Canadian Region affairs and as a director representing the region since 1956 on the NACE board. Dr. Parker, editor of CORROSION, since its establishment in 1945 is well known to most NACE members by reason of her activity with the magazine and her work with technical committees dealing with pipeline corrosion matters.

## 10 More Meetings Planned By Shreveport Section

Ten more meetings have been scheduled by Shreveport Section through 1958 and into 1959. Dates are indicated with the scheduled subject. All meetings are held at the Caddo Hotel, Shreveport beginning with a Fellowship Hour at 6 p.m.:

May 6—Manufacturing Processes for Various Types of Steel Pipe.

June 6—Annual barbecue.

July 1—New Developments in Plastic Pipe.

August 5—Ladies' night.

September 2—Paint Application.

October 7—Discussion of papers presented at regional meeting.

November 4—Deep Ground Beds for Protection of Transmission Lines.

December 2—Student Education Night.

January 6, 1959—Offshore Corrosion Control.

### OFFICERS AND DIRECTORS' PAGE WRONG IN MARCH

Page 16 in the March issue of CORROSION which lists officers and directors of NACE was in error. The new officers and directors listed were those taking office at the last day of the March conference in San Francisco. The page, put in type on advance of the April issue for checking purposes, was inserted in error.

## *Epoxy Resin's Uses Discussed at Chicago Section's Meeting*

"A Modern Approach to Corrosion Control Through the Use of Epoxy Resins in Coatings," a discussion by Harry W. Howard, Shell Chemical Corp., N. Y. was heard by 96 members and guests of Chicago Section at a February 18 meeting. The group also saw a motion picture film of coating applied to a 24-inch gas transmission line with narration by John W. Snider, Crutcher-Rolfs-Cummings, Inc., of Houston.

Mr. Howard's principal points were: Proper surface preparation is essential, with sand blasting preferred. Proper section of proper coating materials is imperative. In discussing epoxies, Mr. Howard stressed the importance of good application, and demonstrated reactions involved in curing. He gave numerous examples of the successful use of epoxy materials in coatings.

Both speakers were occupied for some time answering questions.

R. W. Flournoy, Reynolds Metal Co., was the scheduled speaker at the March 11 meeting on "Use and Application of Aluminum and Aluminum Alloys in the Oil and Chemical Industry."

## Directories' Publication Changes Contemplated

In connection with a pending decision to publish in CORROSION a list of corporate members of the National Association of Corrosion Engineers, a change in the frequency of publication of directories of technical committee and regional and sectional officers is contemplated. Under consideration is publication of one of the three directories a month on successive months in rotation throughout the year.

If adopted the change is not expected to be effective before the May or June issue.

## Atlanta Elects Lehman

Joseph A. Lehman, Electro Rust-Proofing Corp., Atlanta, Ga., has been elected chairman of Atlanta Section along with C. Jay Steel, Steele & Associates, Inc., Atlanta, vice-chairman; James P. McArdle, Jr., American Telephone & Telegraph Co., Atlanta, secretary-treasurer; Emmitte P. Tait, Alloy Steel Products Co., Atlanta, trustee.

## Tidewater Section Elects

Tidewater Section's new officers are George R. Lufsey, Virginia Electric and Power Co., Richmond, Va., chairman; Murray S. Spicer, Chesapeake & Potomac Telephone Co., of Virginia, Richmond; vice-chairman; Otis J. Streever, Newport News Shipbuilding & Dry Dock Co. Newport News, Va., secretary-treasurer.

## Over 200–

Plastic Tapes, Howard D. Segool, Polyken Division, The Kendall Co.

Stainless Steel to Combat Corrosion, G. E. Rowan, Atlas Steels, Ltd., Welland, Ont.

Modern Approach to Corrosion Inhibition Through Epoxy Resins, H. W. Howard, Shell Chemical Corp, N. Y.

# New Orleans Exhibit Arrangements Completed

## October 21-23 Show Dates Scheduled For Conference



FLOOR PLAN for South Central Region's exhibit in the Roosevelt Hotel, New Orleans October 21-23. The exhibit area is located between stairs and elevators and meeting rooms, assuring good traffic. This is the third exhibition held by South Central Region.

Arrangements have been completed for the exhibition to be held concurrently with South Central Region's October Conference in New Orleans. A floor plan has been prepared for the exhibit hall in the Roosevelt Hotel providing for 41 booths. All but six booths are 8 by 10 feet; six booths are 10 by 10 feet.

The exhibition will be open for three days, October 21-23 from 10 am to 5 pm. The conference opens October 20 and closes October 24. Physical arrangements of the exhibit area are such that it is located in the main line of traffic between elevators, stairs and meeting rooms.

Preparations are being made to mail to prospective exhibitors during the latter part of April a floor plan and schedule of applicable rates. Arrangements for the exhibit are being handled at Central Office NACE, where additional information and assistance can be obtained from R. W. Huff, Jr., association assistant executive secretary.

### Third Exhibition of Region

The New Orleans exhibit will be the third held by South Central Region. Exhibits were held in connection with regional meetings in 1956 at San Antonio and in 1957 at Oklahoma City.

As might be expected from the industrial orientation of the area and membership in the region, principal attention at the exhibit is focused on materials and services related to the petroleum industry. Among the 50 companies that have participated in the first two shows are those making instruments, inhibitors, plastic equipment of all kinds, pipe wrapping material and application equipment, paints and painting equipment, galvanic anodes, rectifiers, pumps, valves, engineering services and others.

Location of the conference city in the midst of a rapidly expanding complex of petroleum producing and refining, petrochemical, shipping and other industries is expected to influence participation by many exhibitors. NACE members in Southeast Region, who have a large community of interest with those in the South Central Region are expected to attend the New Orleans sessions.

### New Section Organized

Initial arrangements for holding the October conference in New Orleans were made by the New Orleans-Baton Rouge Section. Recently action has been taken to divide the section into two, a New Orleans section and a Baton Rouge Section. NACE members in the Baton Rouge area have petitioned for recognition as a new section.

In the meantime NACE members in the New Orleans area have proceeded with arrangements for the meeting. A good start has been made on the technical program and much of the work in connection with the entertainment and social side has been done.

Plans are being made for meetings of NACE technical committees during the conference. This has become a very important part of the program at the South Central Region meeting with the number and importance of meetings increasing rapidly.

## Chronological Summary Of Regional Conference

Following is a chronological summary of events scheduled so far for the October 20-24 South Central Region Conference and Exhibition in New Orleans:

Monday, October 20—Technical committee meetings.

Tuesday, October 21—Technical committee meetings. Exhibition open 10 am to 5 pm.

Wednesday, October 22—Technical committee meetings. Exhibition open 10 am to 5 pm.

Thursday, October 23—Technical symposia. Exhibition open 10 am, closes at 5 pm.

Friday, October 24—Technical symposia.

## Baton Rouge Section Sends Recognition Petition

A petition for recognition of a Baton Rouge Section of the National Association of Corrosion Engineers was sent to South Central Region officials after a January 27 meeting attended by 22 persons at Jack's Steak House. A set of regulations was adopted and a meeting scheduled for March 31.

The new section will be the sixteenth for South Central Region and the fifty-sixth for the National Association of Corrosion Engineers. New Orleans-

Baton Rouge Section was organized in 1951 and for several years meetings were held alternately in New Orleans and Baton Rouge.

Temporary officers are P. E. Weaver, Dow Chemical Co., chairman; F. S. O'Brien, vice-chairman and A. H. Tuthill, secretary-treasurer, all of Baton Rouge.

## Oil and Gas Well Groups Will Meet in October

All group committees of T-1 Corrosion of Oil and Gas Well Equipment are scheduled to meet at New Orleans during the South Central Region Conference at the Roosevelt Hotel. An invitation has been issued to other committees to meet also.

The technical program, headed by W. F. Oxford, Jr., Sun Oil Co., Beaumont has been arranged so that technical committee meetings will be held on the first three days and technical symposia presented on the last two days of the conference. In this way many of the conflicts which occur when meetings on similar subjects are held simultaneously will be avoided.

Technical problems related to oil and gas production, marine exposures, pipe lines, utilities and the process industries will be discussed in five symposia. Papers are being scheduled for these symposia now.

# SECTION CALENDAR

**April**

15   Chicago Section. Metallurgical Aspects of Corrosion.

15   Cleveland Section. J. J. Harwood, U. S. Naval Research Laboratory, Washington.

28   New Orleans-Baton Rouge Section. Engineers Club, De Soto Hotel.

28   Tulsa Section. Mayo Hotel.

29   Southwestern Ohio Section. Tour of Duriron Company Plant at Dayton. Developments in Cathodic Protection, M. E. Parker, Houston.

**May**

6   Shreveport Section. Caddo Hotel.

20   Cleveland Section. Speaker: J. F. Ploederl, Wisconsin Protective Coatings Co.

25   Chicago Section. Laboratory Development of Protective Coatings, H. C. O'Brien, Royston Laboratories; Field Evaluation of Industrial Maintenance Coatings, K. Tator.

26   New Orleans Section. Engineers' Club, De Soto Hotel, New Orleans.

26   Tulsa Section. Mayo Hotel.

27   Southwestern Ohio Section, Cincinnati. Refinery Corrosion and Oil Additives.

SOME OF THE MEMBERS and guests at Baltimore Section's January 28 meeting, left to right: Seated, F. E. Costanzo, E. L. Simons, K. M. Huston and N. T. Shideler; second row, Manson Glover, Robert S. Mercer, E. A. Tice, A. S. Levy, W. W. Binger, George E. Best; back row, A. C. Burton, A. F. Minor and J. W. McAmis.

# Advisory Board Organized at Baltimore To Help Guide and Improve Section's Work

A section advisory board consisting of representatives of firms faced with corrosion problems was organized by Baltimore Section at its January 28 meeting. The board will improve acquaintance among its members, provide a nucleus of future section officers, furnish guidance in improving meetings and attendance and membership. First meeting of the board was February 24.

The January meeting was featured by an illustrated discussion of coatings by Norman T. Shideler, Insul-Mastic, Inc., Pittsburgh. Mr. Shideler covered the use of coatings for structures underground and effects of the environment on the coatings.

He also discussed coal tar coatings and a newly-developed coal tar-epoxy ether resin coating, a two component system in which the main body is mixed on the job with catalyst just before application. Coating sets slightly by evaporation and cures by polymerization of the resins. It has less than 10 percent shrinkage on setting, is hard, but retains some flexibility and has excellent adhesion. Aromatic materials affect it only slightly after setting.

### New Officers Inducted

New section officers were inducted as follows: Kenneth M. Huston, chairman; A. Clifton Burton, vice-chairman; James W. McAmis, secretary-treasurer. A past-chairman's certificate was given to B. P. Philibert, 1956 chairman in recognition of his services.

E. L. Simons, General Electric Co., Schenectady, N. Y. regional vice-chairman, then discussed the regional conference proposed for Baltimore in 1959, outlining some of the work to be done. The section will consider holding the conference.

### Joint Meeting Held

The March 11 meeting is the scheduled annual joint session with American Electroplaters' Society and The Electrochemical Society. The dinner meeting was planned for the Park Plaza Hotel, Baltimore. Clarence Sample, International Nickel Co., Inc. was featured speaker on "Corrosion Behavior and Protective Evaluation of Electrodeposited Coatings."

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NACE cooperates with numerous other engineering and scientific organizations all over the world in the collection and dissemination of corrosion control information.

# 1959 NACE Conference to Be Fourth in Chicago
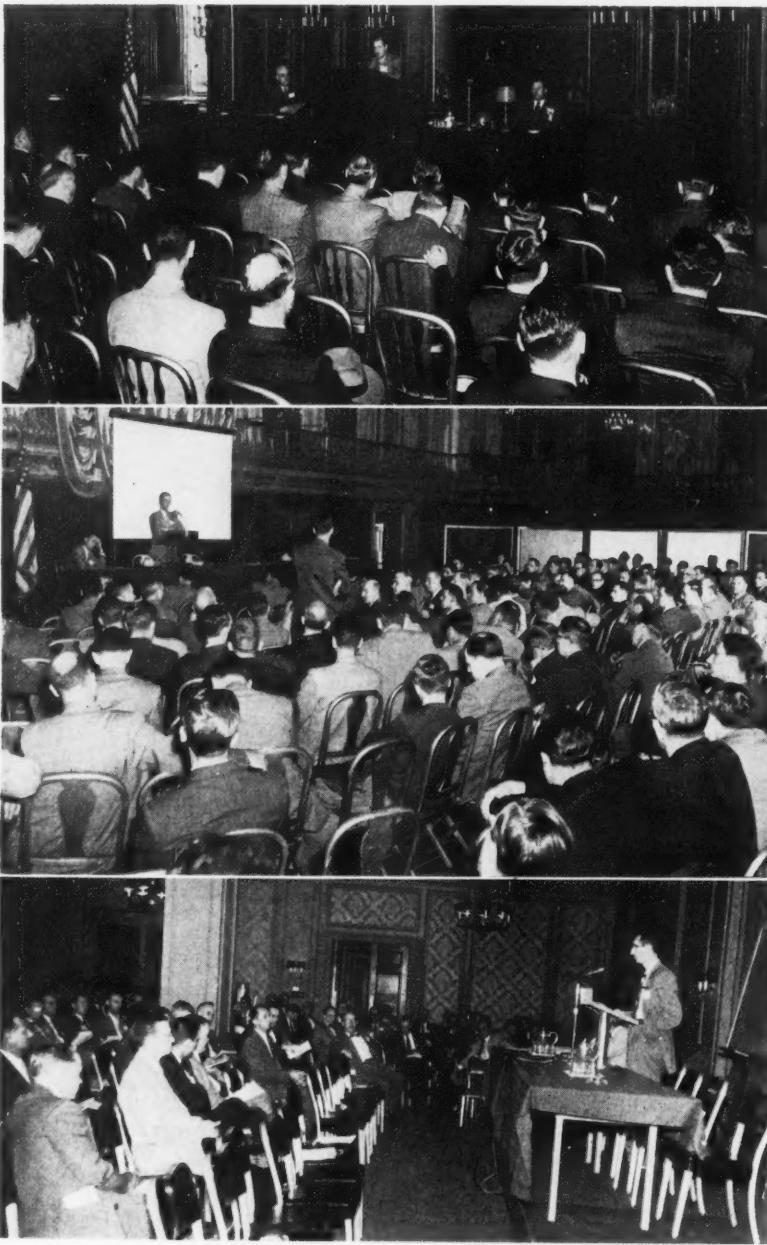


SCENES FROM THREE earlier NACE Conferences at Chicago: Top, general business meeting Monday, April 7, 1947 at the Palmer House. President F. J. McElhatton is at the podium; at his left is H. H. Anderson and at his right Tom L. Holcombe. Center: At Hotel Sherman, March 19, 1953, M. C. Callahan, at microphone; seated at the table, Yale Titterington. Bottom: E. C. Greco presides at a meeting of T-1 Corrosion in Oil and Gas Well Equipment on March 7 during the 1955 conference at Palmer House.

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The 1957 alphabetical subject index to CORROSION's Technical Section occupies four pages.

## *Chicago Exhibit Data To Be Ready in April*

Plans have been made to be available for distribution in April the descriptive literature, contracts, floor plan and other details pertaining to the 1959 15th Annual NACE Exhibition at the Sherman Hotel, Chicago. Firms interested in this exhibition are invited to write to NACE, 1061 M & M Bldg., Houston 2, Texas during the latter part of April, asking for the information.

The 1959 exhibition will comprise about 200 booths located in the Hall of Exhibits and on the mezzanine floor of the Sherman.

## *Exhibition, Technical And Other Sessions To Be at Sherman*

The recently remodeled Sherman Hotel in Chicago will be the location of the 15th Annual NACE Conference and Exhibition.

Enhancing the hotel's advantageous location in the heart of the Loop, is a complete face-lifting for the lobby and extensive interior changes which provide more space and more convenience for conventions and shows. The most outstanding change has been the increase in the exhibit area to a size sufficient to accommodate 200 booths. The Sherman's facilities for handling exhibitions add to its attractiveness to exhibitors who find it easy to get their equipment into and off the exhibit floor.

NACE contemplates an exhibition of approximately 200 booths located in the Hall of Exhibits and on the mezzanine floor. A floor plan, schedule of rates and contracts are expected to be ready late in April.

### Everything in Hotel

Preliminary plans call for all events of the 1959 March 17-19 conference and exhibition to be held at the hotel. This concentration of activities helps save time for all and is considered an asset by exhibitors.

Another advantage about holding the conference in Chicago is the fact that several large hotels are near the Sherman. Registrants that cannot be accommodated at the Sherman, usually are short walking distance away.

Plans have been made also to have all registration and committee meetings as well as social events at the Sherman.

### Fourth Conference at Chicago

The 1959 conference will be the fourth held by NACE in Chicago. It will be the second held at the Sherman Hotel, the previous meeting having been there in 1953.

Arrangements for the sessions will be handled by the large and active Chicago NACE Section. Many members with responsibilities for the meeting will have had previous experience with NACE conferences and this is expected to help make the event a smooth-running affair.

Chicago's location at the focal point for numerous rail and air lines also makes the city a favored spot for conventions such as NACE's. It is near most of the heavily populated sections of the United States and close to the heavily populated section of Canada. This makes it easier for Canadian members to attend the meeting.

### Growing Industrial Area

The rapidly expanding industries of the Chicago area, like those elsewhere along the Great Lakes, have been given a boost by the anticipated completion of the St. Lawrence Seaway. Chicago's port facilities are being expanded in expectation of increased commerce by ocean-going ships that will come up the seaway to dock in the lakes.

The present shallow draft of existing canals limits access to the lakes to ships of comparatively small tonnage.

## Four Regional Meetings Arranged

Four meetings of NACE regions have been scheduled for October and November. Three meetings will be held in October as follows:

5-8 inclusive—Northeast Region, Somerset Hotel, Boston.

15-17—North Central Region, Concinnati.

20-24—South Central Region Conference and Exhibition, Roosevelt Hotel, New Orleans.

Western Region will hold a meeting in Los Angeles November 17-19.

Canadian Region held a meeting in Toronto March 3-4 in cooperation with the Chemical Institute of Canada and the Associate Committee on Corrosion and Rust Prevention.

## Birmingham Meetings Set

Birmingham Section has scheduled meetings as follows at Moulton Hotel:

June 6—Subject to be announced. George H. Speake, Southern Bell Telephone and Telegraph Co., program chairman.

September 5—Mississippi Valley Gas Company's Experience with Deep Sacrificial Ground Beds, by Ralph Hurst. Lawrence R. Hicks, program chairman.

December 5—Providing Cathodic Protection for Large Housing Developments, Ralph C. Cunningham.

## East Texas Section

Corrosion of oil well casing in East Texas is confined mostly to the top 500 feet, M. J. Olive, Arkansas Fuel Oil Corp., Shreveport told 16 members and 36 guests at East Texas Section's February 26 meeting. Mr. Olive, speaking on "Casing Corrosion in East Texas" said acid water, bacterial action and stray currents are the principal causes. Some counter measures were described.

Next section meeting was scheduled for March 25.

## Eastern Wisconsin Section

Eastern Wisconsin Section held a joint meeting February 17 with American Chemical Society and American Electroplaters Society at the Ambassador Hotel, Milwaukee, with approximately 200 members and guests attending. Guest speaker was F. L. LaQue, International Nickel Company, Inc., who spoke on corrosion and protective coatings.

## Rocky Mountain Section

Paul W. Lewis, Bureau of Reclamation, Denver has been elected chairman of Rocky Mountain Section. Other officers named were Herbert L. Goodrich, American Telephone and Telegraph Co., vice-chairman; B. K. Wheatlake, Dearborn Chemical Co., secretary-treasurer and John R. Hopkins, Protecto Wrap Co., trustee.

## South Central 1961 Meeting

Houston's Shamrock Hotel has been selected as the site for the October 24-27, 1961 conference of South Central Region.

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During 1957 over 140 discussions to technical material published in CORROSION appeared.

# GENERAL NEWS

# 60,000 Kw Atomic Power Plant Operating

## Air Pollution Control Papers Scheduled At Atlantic City

Numerous technical papers related to problems associated with air pollution and its control will be given April 24 during the 1958 Industrial Health Conference to be held at Convention Hall, Atlantic City. Five associations in the industrial health field are participating.

Among the papers likely to contain information useful to corrosion workers are:

Air Pollution Control in New Jersey—A Progress Report of The New Jersey Air Pollution Control Commission, William R. Bradley, American Cyanamid Co., Linden, chairman;

Application of Simplified Techniques to Air Pollution Measurement, E. R. Hendrickson, Engineering and Industrial Experiment Station, University of Florida, Gainesville.

Air Pollution Problems in Petroleum Refining, Frank J. Ells, Socony Mobil Oil Co., Inc., Paulsboro, N.J.

Relationships Between Concentrations of Sulfur Dioxide and That of Particulate Matter in Atmosphere, J. Cholak, L. J. Schafer, W. J. Younker and D. Yeager, University of Cincinnati College of Medicine.

Occurence of Phenols in Air and Combustion Products, Ralph G. Smith and James D. MacEwen, Wayne State University College of Medicine, Detroit.

Recent Developments in High Temperature Filtration, J. B. Grahm, Buffalo Forge Co., Buffalo, N. Y. and M. W. First, Newton Centre, Mass.

Sampling of Particulate Matter in Effluent Gases, R. W. Wasser, Public Service Electric and Gas Testing Laboratory, Maplewood, N. J.

Application of Atmospheric Diffusion Formulas, Raymond C. Wanta, Public Service Electric and Gas Testing Laboratory.

Calculation of Air Pollution Potential, Henry C. Wohlers, Stanford Research Institute, Menlo Park, Calif.

Evaluation of Methods for the Determination of Halogenated Hydrocarbons in Air, Evan E. Campbell, Morris F. Milligan, Helen M. Miller, Los Alamos Scientific Laboratory.

Analytical Methods for Phenols in Air, Ralph G. Smith, Robert E. Barrow, Wayne State University.

Radiation Protection Laws and Codes—A Scramble for Action, William A. McAdams, General Electric Co., Schenectady.

## Packaging, Shipping Show

The National Industrial Packaging, Handling and Shipping Exposition will be held October 14-16 at the Coliseum, Chicago. Society of Industrial Packaging and Materials Handling Engineers is in charge.

## BOOK NEWS

**The AWS Bibliographies.** 174 pages, 8½ x 11, loose leaf paper cover. November 5, 1957. American Welding Society, 33 West 39th St., New York 18, N. Y. Per Copy, $5.

A cross-indexed, chronologically arranged list of titles and authors of articles published in the Welding Journal through 1957. Arrangement is variously by materials, methods, industry and techniques. There is no consecutive pagination indicating that supplements will be issued.

## PERIODICALS

**Power Reactor Technology.** 42 pages 7⅞ x 10¼ inches, paper. Prepared by General Nuclear Engineering Corp. for U.S. Atomic Energy Commission. Quarterly. December, 1957, Vol. 1, No. 1. Superintendent of Documents, U.S. Government Printing Office, Washington 25, D.C. Per Copy, $0.55; yearly, domestic, $2.50; foreign, $2.50. Designed to review recent developments in the indicated field throughout the world the first issue considers, among other matters, applications, performance and evaluations, heat transfer, fuel elements, gas cooled reactors and training reactors. Items are summarized from various domestic and foreign sources.

## More Than 50 Papers Scheduled on Corrosion

More than 50 technical papers from authors in 12 countries have been scheduled for presentation during June 5-8, Second Congress of the European Federation of Corrosion at Frankfurt on Main, Germany. The federation's meeting is one of a number to be held during the 1958 European Congress of Chemical Engineering.

Six plenary lectures will be given. Among them are Chemical and Electrochemical Aspects of Reactor Corrosion, by G. H. Cartledge, Oak Ridge; Stress Corrosion of Metals and Alloys, T. P. Hoar, Cambridge, England; Corrosion and Passivation by U. Franck, Darmstadt.

Lectures and discussions under the following headings will be presented: Types and Causes of the Corrosion of Metallic Materials; Fundamentals; water and atmosphere; chemical technology. Protection of Metallic Materials Against Corrosion: Inhibitors, passivators and surface coating agents; plastics, varnishes and paints; electrochemical surface treatment and metallization with various media; miscellaneous. Methods of Testing and Measurement: Planning and rationalization.

Copies of the program of the congress and an invitation to participate may be obtained free of charge from the Congress Business office: Gesselschaft Deutscher Chemiker, Frankfurt (Main), Haus der Chemie, Karlstr. 21.

## Shippingport PWR Unit Incorporates Multiple Safeguards

The Shippingport, Pa. 60,000 kw atomic power station built by Westinghouse Corporation and Duquesne Light Co., Pittsburgh in cooperation with the United States Atomic Energy Commission developed its full design capacity December 23, 1957. Construction of the pressurized water reactor began early in 1955. Duquesne furnished the plant site and a new turbine-generator plant of about 100,000-kw capability which it owns and operates at no cost to the government. Duquesne also operates and maintains the nuclear portion of the plant, assuming all labor costs for up to 100 persons. The company also furnished other services at a value not over $5 millions. Under a 5-year contract it buys steam from the government at a rate of 8 mills a kilowatt hour of net electricity.

The following discussion of the chemistry of the reactor is based on information furnished by scientists and engineers of the United States Atomic Energy Commission, Westinghouse Electric Corp. and Duquesne Light Company.

The chemistry of the pressurized water reactor (PWR) plant incorporates the results of many years of development work on pressurized water reactors in general and on special features of the pressurized water reactor in particular. Problems of corrosion, radiation dissociation of coolant water, fouling of heat transfer surfaces and system activation by impurities settling out of the coolant had to be solved. Ordinary water ($H_2O$), used to transfer heat from the reactor core to the boilers, is demineralized to remove impurities which would have become radioactive by neutron bombardment. To suppress the formation of oxygen from the dissociation of water by the intense radiation in the core, extra hydrogen (25 cc/kg), is maintained in the coolant.

### Coolant Is Inhibited

Corrosion of the stainless steel of the plant is inhibited by raising the alkalinity of the coolant to a range of 9.5 to 10.5 with lithium hydroxide added before start-up. The pH (degree of alkalinity or acidity) is then automatically maintained by using a lithium hydroxide form ion exchanger in a bypass purification system. The high alkalinity also keeps more of the corrosion products in solution and thus reduces fouling of the core and limits activation of the system by corrosion products.

There was also a major chemistry problem resulting from the basic nature and purpose of pressurized water reactor. Production of nuclear power in a pressurized water reactor requires large quantities of source material, which is converted in the core to fissionable material. In the pressurized water reactor

## 60,000 Kw Atomic—

the source material is natural uranium surrounding the core as a blanket.

### Uranium Dioxide Tests Made

Modern practice requires that power plants be used to the maximum possible extent; be operated continuously over long periods; and be readily accessible for maintenance. Thus, fuel element failures must either be very rare or have little impact on operation and maintenance. Radiation damage and corrosion of fuels with high uranium metal content led to an intensive development program on uranium dioxide ($UO_2$), the most likely alternate material.

Many questions had to be answered and tests run before the use of $UO_2$ could be assured and the necessary design data obtained. First, what are the extremes of temperature and environmental conditions $UO_2$ fuel elements can withstand without melting? Second, if failure occurs in an element, is it limited, or does it progress to other elements in the bundle? These questions could be answered only by testing under rigorously simulated operating conditions.

A number of irradiation test facilities or in-pile test loops capable of operation at high radiation levels were designed and constructed. Then $UO_2$ fuel elements containing deliberate defects in the cladding were irradiated at various levels in high temperature water and with various geometries of the tubes and pellets. Unexpected limitations on maximum power without melting $UO_2$ were found, but fortunately these were in excess of the pressurized water reactor design values. Tests also demonstrated that, in the absence of oxygen, $UO_2$ was stable chemically in neutral or alkaline water.

### Failure Progression Checked

To determine if failure progresses from element to element, a bundle of the pressurized water reactor fuel rods was irradiated, with one rod bent so that it touched a neighbor. To make the test more exacting, the cladding on the bent rod was weakened at the point of contact and the rod was filled before testing with a quantity of water (for steam production) sufficient to cause it to rupture at test conditions and temperatures. Even under these very stringent conditions progressive failure did not occur.

Having demonstrated that when used as planned, the $UO_2$ would be stable even if exposed to the coolant through defects in the cladding and that only individual fuel elements would fail, the consequences of operation with defective fuel elements remained to be determined. Accordingly, the release of fission products to the water was measured, and a final corrosion test of one defective element was made over a period of 13 months. The released fission products were found to consist largely of halogens, noble gases and alkali metals, with relatively smaller quantities of the alkaline earths and still smaller quantities of the rare earths. The data were used in evaluating the whole fission product problem in the pressurized water reactor. It was found that the nature and quantities of fission products released would permit the operation of the pressurized water reactor with a large number of failed fuel elements—much larger than is likely to occur within the design lifetime of the core. In addition, it was found that the plant could be made accessible by the use of a continuous ion-exchange purification system and that waste could be adequately disposed of by a system utilizing ion exchange, storage and decay. The systems were designed conservatively on the basis of the data provided by the test program on failed fuel elements.

### Leak Location Methodized

Means for locating leaking fuel elements were developed and incorporated in the plant design. The method utilizes the emission of delayed neutrons from

## High Energy Aviation Fuel On ASME Dallas Agenda

Among the papers presented at the March 16-20 joint Aviation Conference of the American Rocket Society and the American Society of Mechanical Engineers at Dallas were:

High Energy Aviation Fuels, Their Promises and Problems, R. A. Wells, Gulf Oil Corp., Pittsburgh.

Maintenance Engineering for Braniff's Continuous Air-Worthiness Program, E. R. Horton, Braniff International Airways, Dallas.

## Machine Digs Trench, Forms Pipe and Backfills It

Tractor-trenching device which digs trenches for sub-surface drainage systems, forms pipe from plastic sheet and backfills hole will be among new developments introduced to Building Research Institute members at their Seventh Annual Meeting held at Shoreham Hotel, Washington, D. C., April 21-23. Developed by U. S. Department of Agriculture it makes possible reclaiming of swampy, marginal land for development purposes.

## Proceedings on Magnesium In Aircraft Published

Use of Magnesium in Future Aircraft and Missile Structures, and Workable Method for Continuous Welding of Magnesium Proves Highly Efficient are among the papers included in Proceedings of the Magnesium Association's October meeting in New York. Copies of the 160-page booklet are available from the association offices, 122 East 42nd St., New York 17, N. Y. at $5 a copy.

## Environmental Test Engineers Will Convene

Combined Effect of Mechanical and Radiation Stress, by T. C. Helvey, The Martin Co., Orlando is among the papers scheduled to be given during the Second Annual meeting of Environmental Test Engineers. The meeting will be held at Hotel New Yorker, April 17-18.

P. H. Pretz, Ford Motor Co., will discuss Environmental Testing of Automotive Equipment. Both papers will be given April 18.

## Packaging Conference

The First Annual Industrial Packaging Training Conference, to be held April 28-May 10 at Lake Placid Club, New York will consist of a series of lecture-discussion sessions on various phases of industrial packaging. Included among the topics to be considered are preservation and protection.

## Metal Powder Association

The 14th Annual Meeting of the Metal Powder Association will be held at the Sheraton Hotel, Philadelphia, April 21-23. Among the scheduled papers is Applications and Advantages of Hard Surfacing and Corrosion Resistant Surfacing with Alloy Metal Powder, S. Tour, Sam Tour Co., New York.

## Oxidation, Corrosion Theme of Physical Metallurgy Talks

Oxidation and corrosion will be the theme of a session to be held during the Conference on Physical Metallurgy, one of the Gordon Research Conferences. The conference on physical metallurgy will be held June 9-13 at New Hampton School, New Hampton, N.H. under the direction of John Frye, Jr. and Walter R. Hibbard, Jr., respectively chairman and vice-chairman. Theme of the conference is "Microstructures: Their Origin and Influence on Properties."

Scheduled during the oxidation and corrosion session are: Crystal Growth During Oxidation, W. D. Forgeng and E. E. Webb; Sulfurization of Iron, Ralph Condit; Oxidation Nucleation, D. Van Rooyen; Metallic Films, V. J. Albano; Oxidation Kinetics, D. Vermilyea.

Other sessions will be held on special techniques (electron, emission and x-ray microscopy); dislocations studies, precipitation and second phases and deformation and fracture. Morris Cohen will discuss "Brittle Behavior of Steel," in the latter session.

## Lead Industries Meeting

The 30th Annual Meeting of the Lead Industries Association will be held at St. Louis, Mo., April 15-16. American Zinc Institute will meet with the association April 15.

## Research Outlay Grows

Research expenditures at New York University, College of Engineering increased from $2,865,700 to $3,055,400 during 1957 according to findings of 445 faculty members, engineers, scientists and graduate students.

## Materials Handling Session

American Materials Handling Society will hold technical conferences and an exhibition May 8-10 in Los Angeles at the Great Western Exhibit Center.

## 60,000 Kw Atomic—

certain short-lived fission products. Based on detailed observations obtained in irradiation tests, it proved quite successful, indicating traces of uranium in zirconium not previously realized or considered.

A method was evolved for decontaminating systems rendered inaccessible by radioactivity from failed $UO_2$ fuel elements. The success of this development was demonstrated by decontaminating and restoring to use an irradiation loop in which a fuel element had failed under test.

Finally, automatic instruments were developed for determining hydrogen and oxygen levels in the primary coolant; these were incorporated in an analytical and sampling unit for the reactor.

The three-year program, involving the most intensive irradiation test so far carried out on $UO_2$ elements, included laboratory and chemical studies of tremendous detail and scope.

### Positions Wanted

**Three years'** experience cathodic protection—office and field, contracting and supervising. Year drilling fluids experience and sales. B. S. degree business. Age 35. Married. Office and/or field work. Will take foreign. Corrosion, Box 58-3.

### Positions Available

**Paint Technologist**—For research and development in the field of protective coatings with emphasis on high temperature applications. Write Roy W. Hill, Materials Branch, Engineer Research and Development Laboratories, Fort Belvoir, Virginia.

#### Chemist

Research chemist required to lead small group on pure water corrosion in sealed system. Physical chemist experienced in research with interest or experience in metal corrosion preferred but other qualifications might be acceptable if previous experience satisfactory. Salary by arrangement. Please apply in writing to Personnel Officer.

**Ontario Research Foundation**
43 Queen's Park          Toronto, Ont.

**Operations Superintendent**—Opening in medium sized natural gas utility in Midwest for an able graduate engineer or equivalent to supervise construction, maintenance, service on customer premises, appliance installation, metering, pressure regulation and planning system expansion. Liberal benefits. Salary commensurate with experience and ability. State personal and educational qualifications. CORROSION, Box 58-4.

## Adhesives

**Interact,** a material of unidentified composition which is available as wire and in bulk has been tested successfully in joining aluminum to aluminum or similar and dissimilar non-ferrous metals to each other. The material participates in a eutectic reaction with the joined metals at low temperatures. It is made by Intertectics, Inc., Northfield and Forbes Roads, Bedford, Ohio.

## Air Pollution

**Gases** issuing from stacks or other suspected sources of air pollution can be tagged and later assessed by methods involving radioactivity which makes it possible to determine how much of pollution at distances from the source is the result of emissions from a specific plant. The method was developed by Hemeon Associates, 121 Meyran Ave., Pittsburgh 13, Pa. It consists of injecting powdered antimony oxide into gas streams. Tracer samples collected at distances from source are made radioactive after collection.

## Aluminum

**MIG Welding** procedures for aluminum developed by Dept. of Metallurgical Research, Kaiser Aluminum & Chemical Corp., 1924 Broadway, Oakland, Cal. include: Qualiweld, in which the gun is modified to permit introduction down the contact tube directly into the inner core of the arc a mixture of argon and chlorine gas, to eliminate effect of contaminants. Minor measures protect equipment against corrosion and the chlorine is no health hazard because it is only a small fraction of one percent of total shielding gas. In the process Econoweld, nitrogen replaces inert gas in shielding atmosphere and low-flow inert gas is used in the contact tube. The third process, Chlorecon, employs a low flow of inert gas containing a small amount of chlorine down the contact tube with a low flow of inert gas through the nozzle in the outer shield. This process produces code quality welds meeting all bend tests. All processes are patented.

•

**Alclad** (0.032-inch) ogee and half-round aluminum rain-carrying equipment developed by Aluminum Company of America has increased strength and rigidity, new hanging and joining methods eliminating slip joints, straps and inflexible prefabricated miter joints.

•

**Alloy X-385** has been developed by Aluminum Company of America to provide integral bearing surfaces instead of cast-in or specially-assembled bearings and bushings. Loads up to 1500 psi can be sustained; tensile and yield strengths of a typical specimen are 36,000 and 20,000 psi respectively.

## Atomic Energy

**A 5000-thermal** kilowatt swimming pool nuclear reactor built at Sao Paulo, Brazil for Institute of Nuclear Energy

by Babcock & Wilcox is five times larger than any other reactor of this type in existence.

## Coatings—Metallic

**Hortonclad,** Chicago Bridge and Iron Company's process for vacuum cladding of corrosion resistant stainless steels and non-ferrous materials including the high alloys, copper, brass and other alloys is used in producing structural shapes in which heating or cooling channels are incorporated within a heavy base plate. This produces a heated or cooled surface with no obstructing tubing or other protuberances. The base plate is channeled before cladding to form passageways of almost any desired conformation. The clad materials can be rolled to a 12-foot radius in either direction and then re-rolled flat without affecting the bond, either layer, or the channels.

## Coatings—Organic

**R-64 Silicone,** a resin developed by Silicones Division, Union Carbide Corp., 30 East 42nd St., New York 17, N. Y. is expected to find use as a base for aluminum paints on surfaces operating at temperatures in the range 500-1200 F. It is specially designed for cold-blending with alkyd, melamine and acrylic type baking enamels.

•

**ACP Guide,** an 8-page brochure with the various chemical coating conversion for steel aluminum, galvanized iron, zinc and cadmium plated surfaces arranged in tabulated form is available from American Chemical Paint Co., Ambler 1, Pa. Types, purpose, typical metal products treated, scale of production, approximate coating time, coating weight range and equipment notes are given. Relation of the firm's formulations to military specifications on coatings are given also.

## Education

**American Viscose Corporation's** 1958-59 aid-to-education program will benefit 78 colleges and universities in the study of science and engineering. The aid consists of a scholarships and fellowships in the affected schools.

## Electric Switches

**Nylon-Encapsulated** mercury switches developed by Micro-Switch Div., Minneapolis-Honeywell Regulator Co., Freeport, Ill. are designed for use in locations where they are subjected to corrosive liquids or gases. There is no inside space where moisture can collect to cause corrosion or electrical failure.

## Filters

**Nitex Fabrics** available in the United States through Technical Fabricators, Inc., 136 Washington Ave., Nutley, N. J. are made in over 200 different ways for filtering wet or dry particles from 25 to 3000 microns in size. They are made in Switzerland.

## Heat Exchangers

**Karbate** impervious graphite tubes with internal low fins that more than double inner surfaces have been developed by National Carbon Company, Division of Union Carbide Corp., 30 East 42nd St., New York 17, N. Y. The fins twist helically through the tubes, providing turbulent flow at right angles to their longitudinal axis, increasing heat transfer coefficient as fluid velocities increase. They permit designing exchangers with up to half the number of plain ID tubes in corrosive services where internal heat transfer is poor.

## Inhibitors

**Eththylene Glycol** heat transfer medium for use in snow melting systems contains a phosphate-type corrosion inhibitor. It is sold by Dow Chemical Company, under the trade name "Dowtherm SR-1," and is designed to circulate at approximately 140-160 F.

•

**Instantreat,** a rapidly-soluble complex phosphate for low cost protection against lime scale, corrosion and rusty water has been developed by Calgon Company, 323 Fourth Ave., Pittsburgh, Pa. especially for use in solution feeding equipment in small water systems. When used with the Calgon chemical feed pump, the patented phosphate provides a sterile feed solution entirely safe for use in drinking water systems. The pump has no electrical connections or motor.

## Instruments

**Laminagage,** operating on the swept frequency eddy-current principle will measure conducting or non conducting coating thicknesses over the range 0.00005 to 0.007-inch with 10 percent accuracy. It also will locate surface and subsurface cracks in smooth and rough castings, flat stock or plate and tubing. The instrument is made by Gulton Industries, 212 Durham Ave., Metuchen, N. J.

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**Analysis** of ferrous and non-ferrous metals and alloys in 30 seconds is possible using a new direct reading spectrometer developed by Jarrell-Ash Co., Newtonville, Mass. It instantly registers concentrations of up to 30 alloying elements simultaneously on easy-to-read dials.

•

**Corro-dex** battery-operated corrosion testing instruments have single-knob controls and readings indicate corrosion rate directly in micro-inches. Probes of most common metals are available for normal operating conditions and for pressures up to 4000 psi and 700 F. The probe circuit permits assessing corrosion in process without interrupting process streams to install coupons. Bulletin 5502 available from Labline, Inc., 3070-82 W. Grand Ave., Chicago 22, Ill. describes 1958 models.

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**Audio** oscillators developing 15 watts at 750 cps into a 500-ohm load have been

## NEW PRODUCTS

(Continued From Page 86)

perfected by Tinker & Rasor, San Gabriel, Cal. Useful for testing pipe and coating holidays and for locating buried pipe, they operate on a 12-v battery and have a conversion efficiency of better than 70 percent.

•

**A Commercial X-ray** microscope which determines the chemical composition of a specimen is described in a new folder "A High Resolution PMR X-ray Microscope with Electron Microscope Conversion" available from Instruments Division, Phillips Electronics, Inc., 750 South Fulton Ave., Mt. Vernon, N. Y.

### Metals—Ferrous

**Stainless Steel** Division plant of Jones and Laughlin Steel Corp. at Detroit has installed two furnaces making it possible to supply stainless steel bars in a close range of hardnesses to meet customers' specifications. Six types of stainless are being treated.

•

**4-D Wrought Iron** has greatly improved physical and mechanical properties and better resistance to many corrosives, according to A. M. Byers Co., Clark Bldg., Pittsburgh. Improvement was made by substantially increasing the deoxidation of the base metal, increasing phosphorus content and using a more siliceous silicate fiberous material. It is available now and will be produced along with earlier analyses at the same price, the company said.

### Metals—Non-Ferrous

**Tantalum** and columbium will be produced at a pilot plant under construction at Cincinnati by U. S. Industrial Chemicals Co. Rated at a ton of combined metals per month on a one-shift schedule, it is expected to be on stream in April. A USI-developed sodium reduction process will be used, similar to the one at the Ashtabula, Ohio zirconium plant of Mallory-Sharon Metals.

### Non-Metallics

**Six Graphite Blocks** each weighing over $2\frac{1}{2}$ tons have been produced by National Carbon Company for conversion into honeycomb reinforcement in combination with stainless steel panels on the B-58 bomber produced by General Dynamics Corp.

### Pipe Line Equipment

**Maloney Pipe** Line liquid-filled rubber spheres produced by F. H. Maloney Co., Box 1777, Houston are designed for all products lines where an intermediate seal to transmit pressure is desired. Tests show they outwear pigs, will withstand runs of 500 miles before excessive wear losses, follow sharp bends and go through tees more readily. They are available in nominal pipe sizes 4 through 20 inches.

### Plants and Facilities

**Water Service** Laboratories' offices and laboratory have been moved to 169 West Wyoming Ave.

•

**Liquid Hydrogen Sulfide** at the rate of 60 tons daily will be produced at a synthetic hydrogen sulfide plant to be constructed at Moa Bay, Oriente, Cuba by Girdler Construction Division, National Cylinder Gas Co. This first large scale hydrogen sulfide plant to be used in ore processing, will be part of an unusual process developed by Cuban American Nickel Co. to produce nickel from limonite ore.

### Plastics

**Reinforced Epoxy** plastic pipe made of interwoven glass fiber filaments is being produced by Amercoat Corp., 4809 Firestone Blvd., South Gate, Cal. Two to 12-inch Bondstrand pipe, in 20-foot lengths, has plain bell and spigot or flanged ends. Other lengths and diameters up to 40 inches are available on special order. The basic joint is made by placing the spigot end of one pipe into the bell end of the next. An O-ring and a tapered sleeve, both secured with a special adhesive, seal the joint against leakage. Connections for other lines and equipment are provided.

•

**PVC Tubing** shrunk tightly over new or old rolls used in the cellophane, film, textile, paper, chemical and process industries is described in Bulletin RC 9000

# NEW PRODUCTS

(Continued From Page 88)

available from Luzerne Rubber Co., Trenton, N. J.

Teflon tubing connections for equipment handling corrosives are available from Pennsylvania Fluorocarbon Co., Inc., 1115 North 38th St., Philadelphia 4, Pa.

## Tubing

Superior Tube Co., Norristown, Pa. is producing a line of super-alloy tubing in 16 analyses designed not to rupture under stress of 25,000 psi at 1200 F during 1000 hours. Seamless and welded and drawn tubing are offered.

## Wood

Plywood-Molded pipe manufactured by Plycraft, Inc., Lawrence, Mass. is recommended for numerous applications in the chemical, mining and agricultural fields.

# MEN in the NEWS

A. R. Teasdale has been named Director of Advanced Technology at Temco Aircraft Corporation at Dallas. He will direct the efforts of a group of engineering and scientific specialists.

Wesley R. Kegerise has been appointed metallurgist—high temperature alloys by The Carpenter Steel Company, Reading, Pa.

John D. Keane, formerly of the Armour Research Foundation, Chicago, Illinois, has been appointed Director of Research and Executive Secretary of The Steel Structures Painting Council, Pittsburgh, Pa.

Jack H. Kubanoff has joined Fluorocarbon Products, Inc., division of U. S. Gasket Company of Camden, New Jersey as head design and development engineer.

R. O. Barry has been appointed sales engineer by Tube Reducing Corporation. Mr. Barry formerly was district representative for the Industrial Division of the Oliver Corporation and A. B. Farquhar Company, York, Pa.

John Gilbert has been appointed Houston sales representative for Tube-Kote, Inc., Tubular Sales Division. Mr. Gilbert is a graduate of North Texas State College with six years' experience in corrosion control.

Carl Franklin Hoffman, superintendent of Blast Furnace Department of Sparrow Point Works of the Bethlehem Steel Company has been selected recipient of the David Ford McFarland Award for Achievement in metallurgy by The Penn State Chapter of the American Society for Metals.

L. William Kates has been appointed Director of Engineering of Sylvania-Corning Nuclear Corporation, Bayside, Long Island, New York. Mr. Kates joined Sylvania Electric in 1947 as an engineer in the advanced development section of the metallurgical laboratory.

D. W. Rice has been made product sales manager of the conduit division of National Electric Products Corporation and will direct the marketing of the firm's rigid and flexible steel conduit and electrical metallic tubing. Mr. Rice has served the electrical industry for more than 35 years.

A. H. Roebuck is now associated with The Western Company, Midland, Texas. He formerly was with The Continental Oil Company, Ponca City, Okla.

R. D. Scovill has joined Rawdon Myers Agency, manufacturers' representatives of Cincinnati. Mr. Scovill formerly was a district manager for the Moyno Pump Division of Robbins and Myers Co.

Verne C. Kennedy, Jr., sales and engineering executive of a Grayslake, Ill., firm has been named executive director of the University of Oklahoma Research Institute.

W. D. Goad has been appointed sales engineer by Tube Reducing Corporation of Wallington, New Jersey. He holds a BS in mechanical engineering from North Carolina State College at Raleigh.

John H. Corson, formerly manager of The Carpenter Steel Company's research Laboratory, has been appointed manager of the company's Webb Wire Division, New Brunswick, N. J.

Roger M. Blough, chairman of the board of directors of the United States Steel Corporation; Dr. John R. Dunning, Dean of the Columbia University Engineering School and Daniel K. Wright, formerly with General Electric Company are recipients of the year's Stevens Honor Award in recognition of notable achievement.

Frank Batchelor, executive vice president and one of the owner-founders of Quaker Chemical Products Corp., Conshohocken, Pa. was honored recently on his retirement after 28 years. He will continue as a member of the company's board of directors.

John T. Dunton and Howard Hoke have been appointed engineering managers in charge of pipe joining products and service fittings and pipe repair products, respectively in Dresser Manufacturing Division's newly organized Product Engineering Department.

William B. Firman has been appointed marketing manager of Orr & Sembower, Inc. Reading, Pa. Mr. Firman, a graduate of Cornell University, served with Baldwin-Lima-Hamilton and the Worthington Corp. before joining Orr & Sembower.

Robert E. Smith, formerly assistant manager of The Pfaudler Division's chemical sales, has been named vessel sales manager.
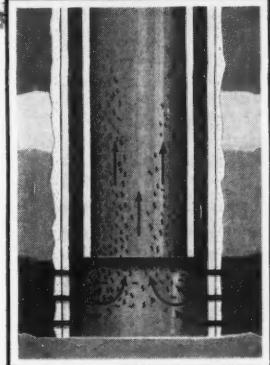
**CORBAN CORROSION INHIBITOR CUTS WELL MAINTENANCE COSTS.** When corrosion forces operating costs up and profits down, pick the inhibitor that does the job best . . . that's Corban®. Field experience has proved that Corban materially extends the life of tubing, pumps and sucker rods on wells producing corrosive fluids. It helps avoid workovers caused by corrosion-damage. Corban coats all the metal surfaces throughout the well which are contacted by well fluids. It is easy to use—does not aggravate emulsion problems.

Corban, a polar-type inhibitor, comes in several forms: "ready-to-use" liquid, concentrated liquid, and in sticks. Also, it is available in several formulas to meet specific well conditions. Call any of the 165 Dowell service points in the United States and Canada for a recommendation of the Corban for your wells. In Venezuela, contact United Oilwell Service. Dowell Incorporated, Tulsa 1, Oklahoma.

*Products for the oil industry* ◆ **DOWELL**

A SERVICE SUBSIDIARY OF THE DOW CHEMICAL COMPANY

# TECHNICAL TOPICS

DIAMOND ALKALI Company produces basic chemicals for industry and agriculture including these: Acids, alkalies, silicates, chlorine, solvents, cement, plastics, chlorine compounds, chromium salts and insecticides. The chemicals are made in 18 plants located in 11 different states with atmospheric conditions varying from the hot, humid climate of the Texas Gulf Coast to the relatively mild climate of the Central states. In most cases, the natural corrosive conditions of the atmosphere and climate are agravated by the chemicals produced in the plants. Hydrochloric acid, chlorine and alkalies are the most common chemicals encountered but each plant condition is different because of design, location and other products produced. In the Northern and Eastern plants the entire operation is usually enclosed in buildings, while the Gulf Coast and Southern operations are built more or less in the open. The two largest operations of Diamond Alkali are located at Painesville, Ohio (30 miles from Cleveland on Lake Erie) and Pasadena, Texas (20 miles from Houston on the Houston Ship Channel).

For many years each of these plants has had a corrosion engineer who has been responsible for corrosion control in his plant. Dissimilarity of plant locations seemed to preclude any overall protective coating standardization.

## Program Started in 1955

In June 1954 the Diamond Alkali Company initiated a company-wide standards program to effect economies in engineering, purchasing and maintenance. Protective coatings standards, as one of the classifications of standards, was started in October 1955. A check made of paint purchases of the 18 plants showed purchases being made from 71 vendors, of 233 different protective coatings, not counting different colors. It was obvious that economies could be made by standardizing protective coatings and reducing the protective coating inventory. At the same time it was necessary to preserve independence in purchasing protective coatings.

Standardization would accomplish the following:

1. Coating application would be improved with resulting economies in maintenance costs.
2. Specifications for protecting new plant construction could be simplified with a considerable savings in engineering man-hours.
3. Standards would give more information to smaller plants without having corrosion engineers.

A "Protective Coating Standards Sub-Committee" was formed, consisting of the following: Central engineering staff engineer, chairman; Painesville Works corrosion engineer, Houston Works corrosion engineer, Cleveland purchasing

★ Condensed from a paper presented by S. W. McIlrath, Diamond Alkali Co., Cleveland, Ohio at a meeting of Northeast Region, National Association of Corrosion Engineers, November 13-14, 1957.

# Protective Coatings Standardization In a Multi-Plant Chemical Operation*

### Abstract
The problem of standardizing coatings in a multiple plant chemical operation is reviewed briefly. A method adopted by one organization is described and reasons for the decisions given. Examples are given of specific standards in use and the company's testing program for new coatings is explained.     **5.4.6**

protective coating buyer, Paint coordinator of Painesville maintenance painting.

In November 1955, the first meeting was held to determine how protective coating standardization for such a large and diversified chemical operation could be accomplished. Use of standards in the

Diamond organization (which is composed of seven autonomous divisions) is not compulsory; therefore, any protective coatings standards must be of such quality that they would be used voluntarily because their use produced savings for the divisions. Many meetings were held before a workable method of writing standards acceptable to all members, plants and divisions was arrived at in June 1956. The method used is novel and is working very well.

## Common Ground Located

First step in organizing the program was to find a meeting ground that was common to all plants. Designating by vendors was impractical because plants were using materials from different sources with the result that no two coatings were the same color. So, standardization of colors was reluctantly adopted.

After much work with many different vendors and the paint laboratory staff standard colors were selected. Six colors: White, black, gray, dark green, tan and cream were designated the workhorse colors. Because they were not identical

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1 Reference

1.1 This standard is to be used in conjunction with General Coating Material Listing Standard DA2-1.1 and General Coating Procedure Standard DE2-1.1.

2 System Explanation

2.1 To provide standard coating systems a combination of letters and numbers has been used to combine material and application specifications to form a coating system.

2.2 This combination of letters and numbers defines the requirements of a protective coating system; identifying the coating required, surface preparation and film thickness.

3 First Letter Designations

3.1 The first letter always designates the coating system to be used as shown on the Material List Standard.

3.2 Letter designations and the applicable standard numbers are:

| | Standard Number |
|---|---|
| A - Asphalt Mastic Coating for Metal | DA2-2.7 |
| D - Decorative Interior Enamel | DA2-4.2 |
| E - Catalyzed Epoxy Coating for Metal | DA2-2.6 |
| H - Exterior Paint for Wood | DA2-3.2 |
| L - Latex Emulsion Coating | DA2-4.3 |
| M - Vinyl Mastic Coating | DA2-2.4 |
| O - Oil Coating for Metal | DA2-2.4 |
| P - Polyvinyl Acetate Emulsion for Exterior Masonry | DA2-5.2 |
| S - Silicone Waterproofing Coating | DA3-5.3 |
| V - Vinyl (PVC) Coating for Metal | DA2-2.3 |

4 Second Letter Designations

4.1 The second letter always designates the Surface Preparation Standard to be used as shown in the Procedure Section.

4.2 Letter designations and the applicable standard numbers are:

| | Standard Number |
|---|---|
| H - Surface Preparation for Metals (SSPC-SP 2-52T) Hand Cleaning | DE4-2.2 |
| M - Surface Preparation for Metals (SSPC-SP 3-52T) Power Tool Cleaning | DE4-2.3 |
| alternate choice SSPC-SP 7-52T) Brush-off Blast Cleaning | DE4-2.4 |
| C - Surface Preparation for Metals (SSPC-SP 6-52T) Commercial Blast Cleaning | DE4-2.5 |
| W - Surface Preparation for Metals (SSPC-SP 5-52T) White Metal Blast Cleaning | DE4-2.6 |
| X - None Designated | |

5 Third Letter Designations

5.1 The third letter designates the metal surface treatment or special instructions.

5.2 Letter designations and the applicable standard numbers are:

| | Standard Number |
|---|---|
| A - Aluminum Vinyl Build Coat | DA2-2.3 |
| R - Rusty Metal Primer | DA2-6.2 |
| W - Wash Prime for Metals | DA2-2.5 |
| X - None Required. | |

6 First Figure Designations

6.1 The first figure always designates the dried film thickness in mils of the prime or sealer coat.

6.2 The dried film thickness designations are:

    0 - None Required
    1 - 1 mil
    2 - 2 mils
    3 - 3 mils

7 Second Figure Designations

7.1 The second figure always designates the dried film thickness in mils of the Build Coat.

7.2 The dried film thickness designations are:

    0 - None Required
    1 - 1 mil
    2 - 2 mils
    3 - 3 mils
    4 - 4 mils

8 Third Figure Designations

8.1 The third figure always designates the dried film thickness in mils of the Finishing Coats.

8.2 The dried film thickness designations are:

    1 - 1 mil
    2 - 2 mils
    3 - 3 mils
    4 - 4 mils
    5 - 5 mils
    6 - 6 mils
    62 - 62 mils or 1/16"

9 System Examples

9.1 Sample system designations and their meanings are as follows:

**OMW-203**

O - Use Oil Coating for Metal as listed on Standard DA2-2.2
M - The surface is to be cleaned in accordance with Standards DE4-2.3 (Power Tool Cleaning) or DE4-2.4 (Brush-off Blast Cleaning)
W - Surface treatment shall consist of the application of Wash Prime Standard DA2-2.5
2 - Apply a 2 mil dried film thickness of the Prime Coat
0 - No Build Coat required.
3 - Apply a 3 m l dried f lm thickness of the Finish Coat

**VCX-102**

V - Use Vinyl (PVC) Coating for Metal as listed on Standard DA2-2.3
C - The surface is to be cleaned in accordance with Standard DE4-2.5 (Commercial Blast Cleaning)
X - No surface treatment required.
1 - Apply a 1 mil dried film thickness of the Prime Coat
0 - No Build Coat required.
2 - Apply a 2 mil dried film thickness of the Finish Coat

**AXX-002**

A - Use Decorative Interior Enamel as listed on Standard DA2-4.2
X - No surface preparation specified.
X - No surface treatment required.
0 - No Primer required.
0 - No Build Coat Required.
2 - Apply a 2 mil dried film thickness of the Finish Coat

**Figure 1—Standard for Coating Systems**

## Protective Coatings—

(Continued from Page 93)

with those already in use, concurrence or management was required.

Red, green, yellow, orange and blue, used in smaller quantities as safety colors are reasonably close to colors produced by most vendors. All colors could be made of readily available pigments.

In specifying the standard colors it was believed desirable to limit, but not restrict, the pigments used in the coatings. Therefore, coating suppliers are allowed a wide choice of pigments with a minimum of restrictions, rather than being restricted by specifications in formulation, which frustrate paint manufacturers' initiative in employing new and improved pigments.

The general standard for protective coating colors requires that pigments used be resistant to acids, alkalies, salts and solvents to the same degree that the resins and/or oils are.

Resins and pigments also must be stable to sunlight and weathering.

### Lead Pigments Excluded

The restrictions in pigmentation of finish coats excludes lead pigments, chalking pigments, pigments of high water solubility and chemically reactive pigments.

Coating quality minimum requirement is that vehicle solids and opacity shall be equal to the suppliers' trade name quality and that all materials shall be supplied in a consistency suitable for brush application but be adaptable for spray application through dilution unless otherwise specified.

To provide a means of designating coating systems, a letter and number

**Figure 2—Coating for Metal Systems**



combination system was devised for each generic type of paint commonly used.

Designations used are indicated in Figures 1 and 2.

The second figure designates the dried film mil thickness of a "build coat" a term used to differentiate it from an intermediate coat. The term "build coat" indicates a material used only as a sandwich between primer and finish coats. Examples are a vinyl mastic covered with a polyvinyl chloride material, or an aluminum sandwich coat, or possibly a special high build material to increase overall film thickness.

The third figure designates dried film thickness of the finished coats. Finish coats with thicknesses over two mils are applied in two separate coats, of which the first—often called intermediate coat—is to be black, or color strongly contrasting to the top coat.

To meet every condition each generic coating material was listed in all possible

**Figure 3—Estimating Coating for Metal Systems**

OIL COATINGS FOR METAL

1 Coating Type

1.1 "Oil Coatings for Metal" are conventional exterior oil enamels for use on metal. These coatings dry by oxidation of the drying oil to a glossy finish, and are composed of: modified synthetic resins of the alkyd, phenolic or epoxy type; pigments, drying oils, driers; and thinners.

2 Surface Preparation

2.1 Unpainted Metal

2.1.1 The entire metal surface is to be cleaned in accordance with method designated.

2.2 Existing Metal (Painted)

2.2.1 Clean all rusted or abraded areas of rust and non-adherent paint in accordance with the method designated.

2.2.2 All dirt, grease and chalking paint is to be removed from the adherent paint by hand wire brushing and solvent cleaning (Standard DE4-2.6), or steam cleaning (Standard DE4-2.9).

2.3 Chemical Contamination

2.3.1 All chemical contamination shall be neutralized and removed in accordance with Standard DE4-2.7.

3 Surface Treatment

3.1 When designated, a 0.3-0.5 mil dried film thickness of Wash Prime for Metal shall be applied by brush or spray in accordance with Standard DE3-4.1 (SSPC-PT 3-53T) Basic Zinc Chromate-Vinyl Butyral Washcoat.

4 Prime Coat Application

4.1 Prime Coat shall be applied by brush in one or more coats to the designated dried film thickness in accordance with General Standard DE3-2.1 (SSPC-PA 1-53T) "Shop, Field and Maintenance Painting".

5 Build Coat Application      Not Required

6 Finish Coat Application

6.1 Finish coat shall be applied by brushing, spraying, dipping or roller-coating the paint in one or more applications to the required dried film thickness in accordance with General Standard DE3-2.1 (SSPC-PA 1-53T) "Shop, Field and Maintenance Painting".

6.1.1 2 mil dried film thickness to be applied in one (1) or more coats of the specified color.

6.1.2 3 mil dried film thickness to be applied in two (2) or more coats. The intermediate coat to be black except when black is to be used for the final coat. Final coat to be of the specified color.

6.1.3 When the finish coat is to be applied in three (3) separate operations the coat next to the prime coat shall be the same color as the final top coat. Intermediate coat to be black except when black is to be used for the final coat.

7 Thinning

7.1 Quality of thinner is to be of the type recommended by the supplier of the oil coating.

8 Film Thickness

8.1 The "Oil Coatings for Metal" can be applied to the following dried film thickness per coat as packaged, without sagging under normal conditions.

8.1.1 Brush Application ----- 1.3 mils

8.1.2 Roller-coat application ----- 1.5 mils

8.1.3 Spray Application ----- 1.5 mils

9 General

9.1 Primer and finishing coats shall be from the same supplier.

CATALYZED EPOXY COATINGS FOR METAL

1 Coating Type

1.1 "Catalyzed Epoxy Coatings for Metal" are chemically cured epoxy resin coatings for use on metal. The coatings dry by evaporation of solvents and the reaction of a catalyst to a tough glossy film having good gloss, chemical resistance. These epoxy coatings are two package materials and must be mixed just before use. One package contains the resin, plasticizer, pigments and solvents and the other either an amine or polyamid solution catalyst. When these two components are mixed, a chemical reaction is set up which results in the curing of the coating. The pot life will vary with the temperature, but in every case it is limited to a few hours.

2 Surface Preparation

Epoxy base coatings in general exhibit very poor adhesion to poorly prepared surfaces. It is therefore considered necessary that the surface preparation be of the highest quality practical to insure that the coating system will successfully provide protection for the metal.

2.1 Unpainted Metal

2.1.1 The entire metal surface is to be cleaned in accordance with the method designated.

2.2 Existing Metal (Painted)

2.2.1 Clean all rusted or abraded areas of rust and non-adherent paint in accordance with the method designated.

2.2.2 All dirt, grease and chalking paint is to be removed from the adherent paint by hand wire brushing and solvent cleaning (Standard DE4-2.6), or by steam cleaning (Standard DE4-2.9).

2.3 Chemical Contamination

2.3.1 All chemical contamination shall be neutralized and removed in accordance with Standard DE4-2.7.

NOTE: Phosphated metal surfaces are not suitable for epoxy coatings in that the catalyst is dissipated by its selective chemical reaction with the complex phosphate compound. As a result, the coating will not cure and the entire job will be totally ineffective. Therefore, hydrochloric acid or acetic acid (vinegar) shall be substituted and followed by a water rinse.

3 Surface Treatment      Not Required

4 Prime Coat Application

4.1 Prime coat shall be applied by spray or brush in one or more coats to the designated dried film thickness in accordance with General Standard DE3-2.1 (SSPC-PA 1-53T) "Shop, Field and Maintenance Painting".

5 Build Coat Application      Not Required

6 Finish Coat Application

6.1 Finish coat shall be applied by brushing or spraying in one or more applications to the required dried film thickness in accordance with General Standard No. DE3-2.1 (SSPC-PA 1-53T) "Shop, Field and Maintenance Painting".

6.1.1 2 mil dried film thickness to be applied in one (1) or more coats of the specified color.

6.1.2 3 mil dried film thickness to be applied in two (2) or more coats. The coat next to the final coat is to be black except when black is to be used as the final color. Each coat shall be of sharply contrasting color to that of the previous coat.

6.1.3 Each coat is to be applied with sufficient thickness to completely "hide" the previous coat.

7 Thinning

7.1 Quality of thinner to be in strict accordance with supplier's recommendations.

7.2 Supplier's recommendations shall be adhered to for normal and maximum reduction.

8 Film Thickness

8.1 Under normal conditions, the epoxy base coatings can be applied to the following dried film thickness per coat without sagging.

8.1.1 Primer    Brush ---------- 1.2 mils    Spray ---------- 2 mils

8.1.2 Finish    Brush ---------- 1.2 mils    Spray ---------- 2 mils

9 General

9.1 Primer and Finish coats shall be from the same supplier.

1 Specifications

1.1 All "SSPC specifications" referred to in these standards are available from the "Steel Structures Painting Council, 4400 Fifth Avenue, Pittsburgh 13, Pa.", or Diamond Alkali Co.

2 Coating Application

2.1 Application of all coatings shall be in strict accordance with the suppliers' printed instructions. When conflict exists between the suppliers' instructions and these standards, these standards shall govern.

2.2 Thinning of the coating shall be held to a minimum to obtain the required dried film mil thickness per coat.

2.3 Mixing of coatings shall be on a mechanical paint mixer where possible. If not, hand stirring and boxing in clean containers shall be done to obtain the same state of homogeneity, that it had when it left the manufacturing point.

2.4 Coating application shall be uniform and free of runs and sags.

3 Film Thickness

3.1 The dried film mil thickness on iron and steel shall be checked with an Elcometer magnetic thickness gage, available from Ferro Corp., Cleveland, Ohio.

3.1.1 The Elcometer shall be zero'd on the cleaned metal using either the .001" or .003" shim under the gage.

3.1.2 Dried film thickness may be checked using either the .001" or .003" shim under the gage to prevent denting the coating.

3.1.3 Coating thickness on thin metals or closer than 1/3" to the edge of the metal shall be checked with a standard micrometer or micrometer depth gage as required.

4 Porosity

4.1 All metal surfaces with a dried film thickness of 5 mils or greater shall be pore free when checked with a Tinker-Rasor Detector M-1.

5 Non-Metallic Surfaces

5.1 A dried film thickness of 2 mils shall constitute complete coverage of the underlying surface.

6 Inspection

6.1 All work shall be inspected by the Corrosion Engineer or qualified supervisor.

## Figure 5—General Coating Procedure

CONFIDENTIAL

         Date _____

Manufacturer _____

Product Name _____

Type of Coating _____

Color _____ Gloss _____ Flat _____ Semi _____ Full _____

NOMINAL COMPOSITION

Pigmentation _____

Total Pigmentation _____ % by Volume

Major Pigment _____

Secondary or Tinting Pigment (s) _____

Total Inerts _____ % by Volume and Identity _____

Vehicle

Total Vehicle _____ % by Volume

Major Vehicle Resin _____

Modifying Vehicle Resin (s) _____

If polyvinyl chloride-polyvinyl acetate copolymer, in what range is polyvinyl chloride constituent?

CHECK ONE: Under 60% ___ 61 to 70% ___ 71 to 80% ___    81 to 90% ___ Above 90% ___

Volatile

Total Volatile Material _____ % by Volume

Weight per Standard U. S. Gallon _____ Lbs.

Viscosity _____ Krebbs Units

Recommended Thinner _____

Reduction   For Spraying - Normal _____ Max _____
         For Brushing - Normal _____ Max _____

Approximate Cost Per Gallon in Ones _____

## Figure 6—Coating Composition Data Sheet

### Figure 4—Coating Application Procedures

# Protective Coatings—

(Continued from Page 94)

combinations that normally would be used.

These systems can be expanded or diminished at will and new systems can be made up to meet special requirements.

### Recommended by Engineer

Use of the systems is generally recommended to the painting force by either the corrosion engineer or other person responsible for painting. When a coating system has been stipulated this information is included on the drawings.

The purchasing department or the plant may select materials of any supplier depending upon location and competitive prices. It usually is stipulated that the primer be purchased from the same supplier as the finish coat.

Different quantities of paint usually are required in painting new steel as contrasted to rusted steel. Also, the quantities of paint usually will be different depending on whether application is by spray or brush. Therefore, if the estimator knows how the paint will be applied, he will be able to arrive at a fairly accurate estimate of the number of gallons required.

Application specifications or estimates are provided for each generic type of coating used.

In Figure 3 a short description is given the contractor of what oil and epoxy catalyzed coatings for metal are and a general standard for metal coverage and thinners is itemized. Surface preparation already has been designated in the system's second letter. Structural Steel Painting Council Surface Preparation Specifications are used throughout for simplicity and availability.

Therefore, if the method designated for surface preparation is mechanical cleaning, the SSPC specification for mechanical cleaning would be attached. If the metal to be painted is an existing job, which has been painted previously, the contractor shall clean all rusted areas and prime and in addition, remove any dirt, oil, grease and chalking paint which may be on the balance of the job, before top coating.

Figure 4 gives data on application procedure for oil and catalyzed epoxy coatings while Figure 5 gives general instructions on coating application and the method used to check film thickness.

In order to keep abreast of improved paints a testing program is conducted. When a new supplier contacts the purchasing department he is requested to fill out a confidential data sheet.

### Data Sheet Is Confidential

A new type of confidential data sheet was adopted recently which is acceptable to all suppliers. This requires only pertinent information believed necessary to determine if the coating meets the pigment and solids content restrictions.

Data on percentage by weight makes it easier to check the relation of solids content to the cost per mil of thickness by nomograph. After these data sheets are received, the committee screens them for cost per mil thickness and places them for testing in their generic type.

An interesting discovery made while developing these standards was that while much paint testing had been done to determine the best coating for an area, results still did not permit ready comparison of coatings of the same generic type. So, generic types are now being tested against each other, i.e., oils will be tested against oils and vinyls against vinyls, mastics against mastics, to determine which supplier's material is superior. When a material is shown to be superior to those already in the standard, it will then replace a like material or be added to them.
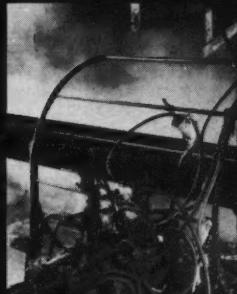
# Now, lay coated pipe without "Special" handling
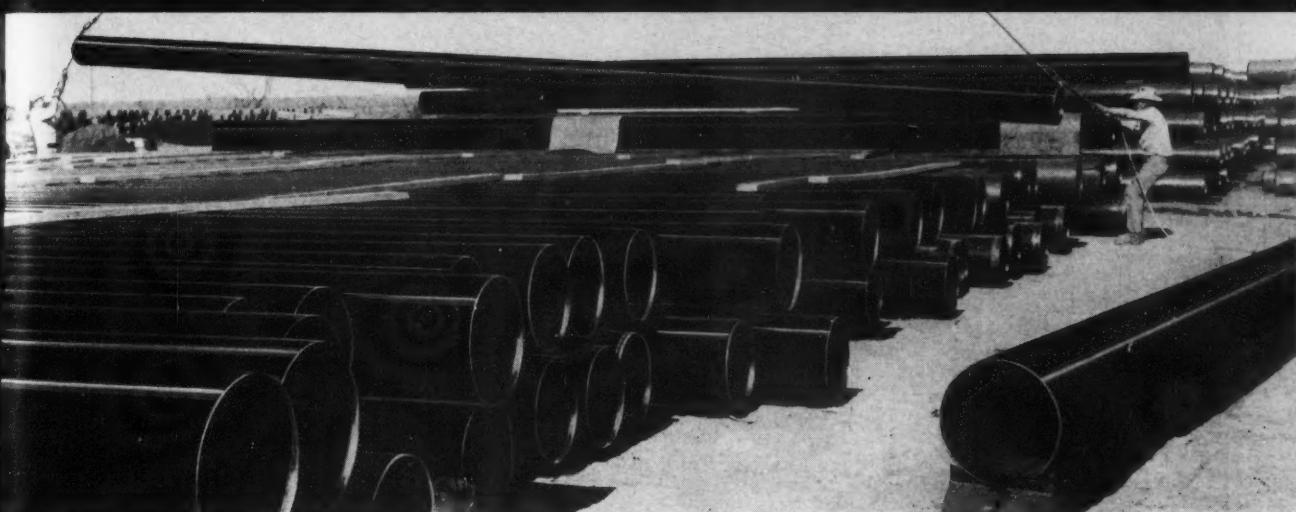
ABOVE: 16-inch pipe being spray-coated for use in new Transcontinental Gas Pipe Line Corp. gas-gathering system near Tilden, Texas.

Save up to 20 per cent in laying costs on large-diameter pipelines. Spray—coat pipe with Copon Arocoat before installation. Then, haul it, stack it, bend it and lay it with little more care than you would use for bare pipe. Tough Copon Arocoat coatings will survive these operations without chipping or cracking, and Copon Arocoat can be applied to welds with an ordinary paint brush.

A combination of epoxy and coal tar resins, Copon Arocoat coatings provide superior corrosion control. They will not deteriorate in the ground . . . remain tough and elastic . . . and are unaffected by temperature extremes. Successful applications include submerged, buried and exposed transmission lines.

Get complete information on Copon Arocoat, industry's newest weapon in the fight against rising costs of corrosion. Write today to the Copon Associate located nearest to your city.

# Impressed Current Anodes Installed
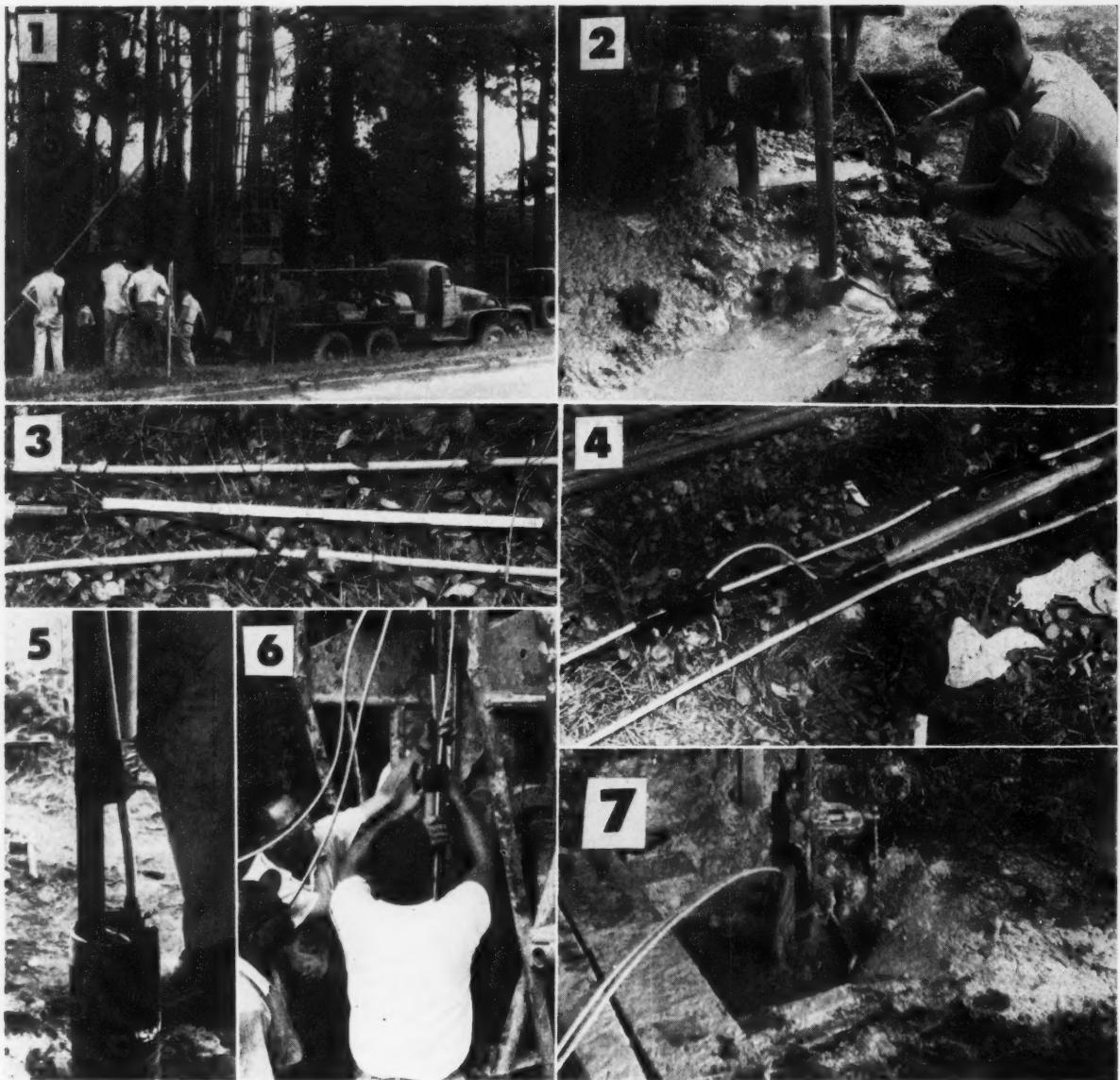


Figure 1—Water well rig set-up ready to spud in.

Figure 2—Four-inch surface casing as drilling mud is circulated out the top where cuttings samples are taken for determination of resistivity trend.

Figure 3—Anode pigtail attached to header cable.

Figure 4—Anodes and header wires insulated for protection.

Figure 5—Anodes being attached to 1" pipe.

Figure 6—Notched fitting on top of casing to eliminate header wire damage.

Figure 7—Swivel connection pumping water slurry of coke breeze to bottom of hole.

# 1-Ohm Resistance in Ground Beds

IN a distribution system, where electrical power for rectifiers cost 4 cents per kilowatt hour and current requirements are high, it is necessary to locate the lowest possible ground resistance for the installation of cathodic protection ground beds. When resistances of low order are to be found only in close proximity to other structures or at depths of from 150 to 450 feet it is necessary to develop an economical means to install a reliable anode system at these depths.

Willmut Gas and Oil Company, Inc., a distribution company serving 13,000 customers in South Mississippi has developed a method for installing and back-filling anode beds at these depths. To date three beds have been installed at depths from 290 to 350 feet with resulting resistances of one ohm to ground and lower.

This article describes the manner in which these beds are installed.

### Introduction

Original distribution systems of the company were installed in 1931 and 1932. The systems are essentially bare,

★ A paper by Joe F. Tatum, Willmut Gas & Oil Co., Hattiesburg, Miss. at the 14th Annual Conference, National Association of Corrosion Engineers, San Francisco, Cal., March 17-21, 1958.

# And Back-Filled at Depth of 350 Ft.*

### Abstract

A method is described for installing high silicon cast iron ground anodes and back-filling with coke breeze or graphite 350 feet deep where power costs are high and where location or low resistance soil is hard to find. Resistances of one ohm to ground are obtainable readily by this method with soil resistances on the order of 2000 ohms per centimeter. Gas blocking with a 10 to 20 ampere drain has not occurred in these installations in a year's operation.

Benefits such as improved current distribution, low interference effect and installation savings are discussed. Protection is extended to approximately 40,000 square feet of poorly coated pipe surface within a ½ mile radius of groundbeds.

5.2.3

having been coated upon installation with a cold applied asphalt base paint. The pipe was cleaned with a wire brush before application and no attempt was made to remove grease and mill scale. This has resulted in very low paint adhesion. In 1946 the leakage ratio was 8.48 percent of volume, leaks were being repaired but no provision was made for corrosion control. The first cathodic protection installations were made in 1947 by the application of 17-lb. magnesium anodes at "hot spots". Since that time the corrosion program has grown constantly and is coordinated with line repair with the results that when leaks are repaired, cathodic protection is applied to reduce recurrence. The leak ratio has dropped to a point that savings in gas shrinkage alone have more than offset the entire cost of the corrosion control program. Leakage on the distribution systems in 1956 was reduced to the low figure of .05 percent.

In 1954 the first rectifier ground bed installations were made in the conventional manner after an exhaustive search for low resistance soil on the surface (in the area searched this means 3000 to 1000 ohms per cc). Low resistance soils located were often in places immediately adjacent to neighboring structures. Surveys indicated that the hazards of interference currents were so great that either it would be necessary to drain small amounts of current at many locations or a method would have to be developed to locate suitable ground beds at a remote distance from the foreign structures.

### Low Resistance Strata Located

By investigation of water well logs and information from well drillers it was ascertained that a low resistance clay stratum generally underlies the area at depths between 150 to 450 feet. To take advantage of this stratum the first deep ground bed was installed at 320 feet using five 10-foot high silicon cast iron anodes. No back-filling was applied because it was thought to be impossible at these depths. This resulted in a ground bed with 2-ohm resistance to ground, not considered to be sufficiently low.

To lower this resistance a method was developed to back-fill the anodes with coke breeze. This method has been used to install three ground beds at depths from 290 to 350 feet with resulting resistances 1 ohm to ground or less.

### Installation Method

A water well rig was used to drill a 6-inch hole using a regular Bentonite

drilling mud as a circulating medium. A 4-inch casing was inserted in the hole consisting of one joint to block surface water and prevent hole sluffing. Beneath this casing samples were taken of returned cuttings every 10 feet. The washed samples were put into a soil box and earth resistance trends were determined. This method of determining soil resistance was inaccurate at best because of the dilution of the samples with drilling mud and other contaminants. Resistance varied from 1500 to 1800 ohms and was believed to be less than the actual soil resistance. To get an idea of the effect of the con-

taminants on the soil resistance three checks were made as indicated in Table 1.

**TABLE 1—Variations of Resistance of Soil Saturated With Drilling Mud**
Ohms Per Centimeter

| Sheppard Rod Reading | Soil Box Reading | Soil Box Reading[1] |
|---|---|---|
| 1,000.......... | 1,360 | 1,150 |
| 2,500.......... | 2,920 | 814 |
| 10,000.......... | 8,320 | 2,800 |

[1] Sample saturated with drilling mud.

## Impressed Current—

These checks showed the effect of contaminants in lowering the resistance as measured in the soil box. Drilling was continued until it became apparent that the main body of clay had been passed, provided this took place at below the 200-foot level. It was anticipated the hole could be drilled to a maximum depth of 500 feet. In all cases suitable clay strata were located above 350 feet but in no case was the clay strata homogeneous but broken periodically with streaks of sand and gravel.

### Anode Systems Described

After maximum depth was reached, drilling mud was circulated through the hole until all caving had subsided and the hole was clean. Then ten 5-foot silicon cast iron anodes were installed in each bed. They were connected alternately to each of two No. 4 polyethylene-polyvinyl wires. Bottoms and tops of the anodes were tapped to decrease end erosion effect. Two wires and alternating tapping were used so that only half of the ground bed would be affected if one wire was damaged.

After the anodes were strung they and the header wires were attached to a 1-inch pipe which was lowered into the hole with the anodes. A 4-prong guard at the leading end of the pipe centered it in the hole. The end of the pipe was plugged with a bolt and washer tapped so it could be blown off with pump pressure. A spacing of 2 feet between anodes ends was maintained. The 1-inch pipe threaded connections were made tight to the length of the anode string (in the case of 10-foot anodes at 2-foot spacing this means 60 feet) and at the end of this string of tight connections a long threaded coupling was left loose. All pipe joints above the loose coupling were made secure.

The pipe and anodes were carefully lowered into the casing. A slotted pipe was used at the top of the casing to prevent damage to the header wires while lowering the anodes. When the anodes reached the bottom of the hole a slurry of coke breeze (which had previously been sifted through a regular household screen) and water was mixed in the mud pit and pumped through the swivel connected to the 1-inch pipe. This slurry was pumped in until it flowed from the top of the hole. Then the pipe was unscrewed at the loose coupling and the excess was pulled and recovered for future use. The pipe served two purposes: To hold the anodes in approximate position until the settling of the backfill in the hole occurred and as a means of installing the backfill at the proper place.

Immediately after installation these ground beds had a resistance to earth of 2-2½ ohms. This resistance gradually trended downward with time and 24 hours later the anode-to-earth resistance had dropped to 1 ohm or less indicating the coke breeze back-fill was settling around the anodes. These ground beds have been in service for a year and there has been no evidence of gas blockage and no increase in anode-to-earth resistance. To finish the installation either a 10 or a 20 ampere oil-immersed rectifier was installed. Time polarization and current potential studies show that one ground bed installed in this manner draining 10 amperes will provide adequate protection to about 40,000 square feet of poorly coated pipe surface within a ½-mile radius under average soil conditions. The amount of current throw obtained depends upon the longitudinal resistivity and contact resistance of the pipe drained.

Extensive testing on foreign structures involved has failed to show any evidence of anodic interference. Although a cathodic gradient exists it apparently has negligible effect in that interference currents cannot be detected on the neighboring structures.

### Conclusions

The following conclusions were drawn from these installations:

1. Remoteness of the ground bed makes for efficient current distribution and remote locations in distribution systems are often hard to obtain except by this method.

2. Interference currents on neighboring structures are generally reduced to a negligible value.

3. With the ground bed underneath the pipe some of the most potentially corrosive areas are closest to the current source.

4. Installation costs are no greater than for a conventional surface installation.

5. Engineering time is greatly reduced by eliminating the surface search for low resistivity soil.

6. Ground beds can be placed at the center of an area to be drained rather than being dictated by the availability of suitable locations.

7. No expense is involved in securing right-of-ways as the ground bed generally can be placed directly below the pipe.

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## Technical Topics Scheduled for May

Diminishing Cost Ratio Favors Baked Pipe Coatings

Surface Preparation Is Key to Coatings Life on Underwater Structures

Service Life and Relative Cost Data on Reinforced Epoxy Pipe

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# TECHNICAL REPORTS

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## 3. CHARACTERISTIC CORROSION PHENOMENA

### 3.8 Miscellaneous Principles

**3.8.4, 4.3.2, 6.3.10**

Kinetic Study of the Corrosion of Nickel in Sulfuric Acid (Technical Report No. 20). CHARLES H. PITT AND MILTON E. WADSWORTH. Institute for the Study of Rate Processes, Utah Univ., Project NR-051-192, Contract N7-onr-45103, Jan. 31, 1957, 24 pp.

The corrosion of nickel in sulfuric acid solutions in the temperature range of 75 C to 125 C and from 0 to 600 psi partial oxygen pressure was investigated. The variation of rate as a function of agitation, time, acid concentration and partial pressure of oxygen was determined. The rate was found to be linear over the range of time investigated under the experimental conditions of this study and varied directly with oxygen concentration. A systematic variation of acid concentrations using buffered solutions indicated a process in which the undissociated sulfuric acid molecule plays an important part. Calculation of the activation energy for the process gave a value of approximately 4 kcal for the rate of determining step. The rate determining step was considered to be the adsorption of oxygen on a site containing adsorbed sulfuric acid. (auth) —NSA.                    13853

**3.8.4, 4.7, 6.4.2**

Electronographic Investigation of Oxide Film Forming on Liquid Aluminum and Its Alloys. (In Russian.) M. V. MALTSEV, YU. D. CHISTYAKOV AND M. I. TSYPIN. Kalinin Moscow Inst. of Non-Ferrous Metals and Gold. *Bull. Acad. Sci., USSR* (Izvest. Akad. Nauk, S.S.S.R.), Physical Series, 20, 824-826 (1956) July.

Investigations were made of the oxide film γ-aluminum oxide forming in molten high-purity 99.9% aluminum binary alloys: aluminum-copper, aluminum-magnesium, aluminum-zinc, aluminum-manganese, aluminum-silicon, aluminum-iron, and some more complex commercial aluminum alloys containing beryllium, lithium, magnesium, calcium and strontium. Nichrome rings were used to skim the film from the surface of the molten bath of aluminum and its alloys at 660, 670, 680, 690, 700, 800, 900, 1000 and 1100 C. It was found that oxide films formed during concentrations of more chemically active metals (lithium, beryllium, magnesium, polonium and strontium) had a two-phase structure and depending on the nature of the oxides, the film of the base alloy became either stronger or weaker, thus, improving or reducing the anticorrosion resistance of the alloy.—NSA.    13919

## 4. CORROSIVE ENVIRONMENTS

### 4.2 Atmospheric

**4.2.1, 3.5.9**

Atmospheric Corrosion of Metals at Low Temperatures. (In Russian.) A. A. DYCHKO AND K. A. DYCHKO. *J. Applied*

*Chem., USSR* (Zhur. Prikladnoi Khimii), **30**, 255-263 (1957) Feb.

Effect of temperature on atmospheric corrosion. Critical temperature of —25 C is found; below this point, the process of atmospheric corrosion is much slower.—BTR.                                    14300

**4.2.1, 5.9.4, 6.4.2**
**Evolution of the Appearance of Anodized Aluminium Surfaces as a Function of Time and Attack by Various Atmospheres.** (In French.) FRANCOIS FLUSIN. *Rev. Aluminium,* **34**, No. 243, 525-530 (1957) May.

Some isolated cases of atmospheric attack on carpentry work, roofs and architectural panels made of aluminum-silicon-magnesium or aluminum-magnesium-silicon alloys and their causes are studied. The defects observed are classified as stains, pitting and a white powdery deposit. It is said that if anodizing is carried out properly it provides satisfactory protection from weathering.—ALL.                                    14293

**4.2.3**
**Dew-Point of Flue Gas and Flue Gas Corrosion.** (In German.) W. GUMZ. *Brennstoff-Warme-Kraft,* **9**, 118-125 (1957) March.—BTR.                    14064

**4.2.3, 4.3.3, 5.8.2**
**A Liquid Additive to Limit Oil Ash Corrosion.** R. S. NORRIS. *Corrosion,* **13**, No. 7, 123-124, 126 (1957) July.

The problem of vanadium and sodium corrosion of fire side of boilers and of gas turbines and Diesel engines is reviewed briefly and some explanation of the growing severity of the problem given. Elements of the theory whereby reduction of corrosion by increasing the melting temperature of oil ash residue are explained and some of the materials used for this purpose named. Advantages and efficiency of using an oil soluble aluminum salt inhibitor over inhibitors introduced as slurries are described and some experimental results tabulated.                                    14240

## 4.3 Chemicals, Inorganic

**4.3.3, 4.2.3, 5.3.2**
**Aluminum Coating on Stainless Steel.** J. E. SRAWLEY. U. S. Naval Research Laboratory, October, 1956, 41 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 121487).

Coatings of hot-dipped aluminum on Type 310 stainless steel did not impart substantially better resistance to fuel-ash constituents than the uncoated steel, it was determined by this research. Tests of the aluminum coatings were part of a continuing search for materials which will withstand corrosive attack of residual fuel-oil ashes on Navy boilers and gas turbines. Although superior resistance had been predicted for the coatings, limited testing indicated that no useful protection was gained against contamination by vanadium pentoxide, the corrosive agent used in the tests.    13385

**4.3.6**
**Progress Report on Corrosion Tests in UCl₄.** DONALD R. MASH. Tennessee Eastman Corp. U. S. Atomic Energy Comm. Pubn., AECD-4033, May 26, 1945 (Declassified January 10, 1956), 13 pp. Available from: Office of Technical Services, Washington, D. C.

The corrosion resistance of Hastelloy and various types of stainless steel to solid and vaporized UCl₄ was deter-

mined. Tests were run for 150 hours at 500 C and for 12 hours at 700 C. Penetration and weight loss were determined and all samples were examined microscopically with and without a bend test. Hastelloy was found to be the most corrosion-resistant of the materials tested.—NSA.                                    13284

## 4.4 Chemicals, Organic

**4.4.3, 4.6.4**
**Some Aspects of the Corrosion Processes of Iron, Copper and Aluminum in Ethylene Glycol Coolant Fluids.** P. F. THOMPSON AND K. F. LORKING. *Corrosion,* **13**, No. 8, 531t-535t (1957) August.

The corrosion potentials of aluminum, iron and copper, the principal metals in coolant systems, were measured in glycol-water solutions. The effect on the corrosion properties of these metals of the addition of triethanolamine phosphate, formerly used as a corrosion inhibitor in glycol coolants, was studied. It was shown that the copper ions produced by corrosion of copper are stabilized by triethanolamine phosphate. The copper went into solution as a blue cuprammine complex, which remained stable until it reached iron or aluminum surfaces where it was deposited, causing localized corrosion.    14006

**4.4.6, 3.5.11, 8.4.5**
**High Velocity Corrosion Study in Organic Media (Technical Report No. 54).** K. R. BARKER AND J. W. MAUSTELLER. Mine Safety Appliances Co., Callery, Pennsylvania, Contract Nobs-65426, February 27, 1957, 31 pp.

Corrosion tests in organic coolants were conducted in a pumped corrosion test loop designed for test exposures at four velocities, 0, 4, 9 and 27 ft/sec. Two 30-day runs were completed using biphenyl coolant at a temperature of 800 F and surge tank pressure of 300 psig. Samples of zirconium-7 wt.% uranium, Zircaloy 2, Zircaloy 3, hafnium, Type 304 stainless steel, two Alcoa aluminum alloys and carbon steel were placed in the several velocity sections of the loop. Zirconium, zirconium alloys and hafnium were severely hydrided but the steels and aluminum alloys were relatively unaffected. The effect of velocity was apparent only in the zirconium and zirconium alloy results. Performance of the various components is discussed. (auth).—NSA.                                    14149

**4.4.6, 7.5.5**
**Corrosion in Light Oil Storage Tanks.** E. H. TANDY. *Corrosion,* **13**, No. 7, 427t-432t (1957) July.

The most important factors governing corrosion rates in oil storage tanks are solubility of oxygen in the oil, rate of working, type of roof used, vapor pressure of the oil and location of the tank (climatic conditions.) Data are given to show the relationship between stocks contained in tanks versus corrosion rate and size and location of tanks versus corrosion rate. A corrosion mechanism is considered briefly. Corrosion control measures discussed include gas blanketing, inhibitors, breathing systems and protective coatings. Other topics considered include corrosion below the liquid level, vapor space effects, temperature effects and plate thickness corrosion allowance.                    13924

**4.4.7**
**Investigation with Radioactive Indicators of the Reaction Mechanism of Thiophosphoro-Organic Additives to Oils.** (In Russian.) G. V. VINOGRADOV,

M. M. KUSAKOV, P. I. SANIN, YU. S. ZASLAVSKY, E. A. RAZUMOVSKAYA, A. V. UL'IANOVA AND D. V. RIABOVA. Khimiya i Tekhnologiya Topliva (*Chemistry and Technology of Fuels*), No. 6, 14-20 (1956) June.

Antiwear properties of additives. Effects of presence of phosphorus and sulfur.—MR.                                    13704

## 4.6 Water and Steam

**4.6.5, 6.4.2**
**Aluminum Alloys for Handling High-Purity Water.** W. W. BINGER and C. M. MARSTILLER. *Corrosion,* **13**, No. 9, 591t-596t (1957) Sept.

Aluminum alloys have been used for more than 20 years for storage and distribution systems handling distilled water. Recently, it became possible to investigate experience with some 30 distilled water systems which had been in use for various periods of time up to 24 years. Many of these systems had been made entirely of aluminum. Several were composed entirely of tinned copper or brass and others were made up of a combination of materials including aluminum.

Results indicate that aluminum alloy storage tanks, tubing, fittings and valves are highly satisfactory for handling distilled water and do not cause significant contamination of the water being handled.

The increased use of the ion exchange method for purifying water has required equipment fabricated from materials in which such a water could be handled with a minimum of pick-up and discoloration. Since many processes require large quantities of a water of very low total solids content, it was natural to consider aluminum alloys for the fabrication of storage tanks and piping for handling demineralized water.    14191

**4.6.7, 5.4.8, 5.2.1**
**Paints to be Simultaneously Applied with Cathodic Protection of Metal Structures Under Fresh Water.** (In Japanese with English summary.) MASAO GOTODA and YASUSHI SATO. *J. Electrochem. Soc., Japan,* **25**, No. 4, 208-213 (1957) April.

Combination of coating with cathodic protection is an effective way of protecting under-water structures. Since the paint coats under protective current are exposed to accelerated deterioration through cathodic reaction due to alkali formation and electroosmosis, the paints to be applied for this particular purpose should be especially water-proof, alkali-resistant and highly adhesive.

There are a considerable number of studies reported on such paints for sea-water use, but very few are to be found for fresh-water use. Some ten kinds of paints were put to test in order to choose the most suitable one to be used in combination with cathodic protection on hydraulic power station structures and drinking-water receptacles on the train. Deterioration test was made in tap water under protective current. Then the potential distribution on the surface of a coated steel piece attached with magnesium anode was measured and the results were examined for their relation to the conditions of paint coat.

Test procedures and results are given. Included in the tests were oil-soluble type, bituminous, coumarone-indene resin, polyvinyl chloride and chlorinated rubber paints.—JSPS.                    14181

## 4.7 Metallurgical Effects

### 4.7, 2.3.4

**Corrosion and Metal Transport in Fused Sodium Hydroxide. Part I. Experimental Procedures.** G. PEDRO SMITH, M. E. STEIDLITZ and E. E. HOFFMAN. *Corrosion*, 13, No. 9, 561t-564t (1957) Sept.

Experimental techniques are described for studying corrosive reactions and metal transport in fused sodium hydroxide at temperatures up to 815 C. The apparatus described is designed for small-scale testing.

Some of the factors which previous research has shown to be of importance in the design of fused hydroxide corrosion tests are reviewed. Test methods discussed include the capsule, cold finger and controlled-atmosphere test techniques. 14198

### 4.7, 6.3.10

**Corrosion and Metal Transport in Fused Sodium Hydroxide. Part II. Corrosion of Nickel-Molybdenum-Iron Alloys.** G. PEDRO SMITH and EUGENE E. HOFFMAN. *Corrosion*, 13, No. 10, 627t-630t (1957) October.

Studies were made of the corrosion by fused sodium hydroxide of nickel-rich alloys whose constituents were nickel, molybdenum and iron exposed at 815 C for 100 hours. The reaction mechanism was found to involve the selective removal of iron and molybdenum from solid solution with nickel and a resultant formation of subsurface porosity. In most cases this porosity was shown to occur in the form of elongated pits which frequently followed tortuous paths and intersected to form a maze of subsurface channels.

Alloys of nickel, molybdenum and iron containing at least 70 percent nickel showed more resistance to corrosion by sodium hydroxide melts at 815 C than any other alloys tested. 14260

### 4.7, 8.4.5

**Activity Transport in Sodium-Cooled Systems.** FRED G. HAAG. Knolls Atomic Power Lab. *Nucleonics*, 15, No. 2, 58-61 (1957) Feb.

An experiment is described in which the transfer rates of $Co^{60}$, $Mn^{54}$, $Ta^{182}$, $Fe^{59}$ and $Cr^{51}$ from stainless steel by liquid sodium are determined. The effect of temperature, oxygen concentration and various inhibitors is reported.—NSA. 13906

### 4.7, 8.4.5

**Alplaus Surveillance Program. Progress Report No. 2.** E. G. BRUSH. Knolls Atomic Power Lab. U. S. Atomic Energy Comm., Pubn., KAPL-M-EGB-4, August 29, 1952 (Changed from Official Use Only June 26, 1956), 9 pp. Available from Office of Technical Services, Washington, D. C.

Type 347 stainless steel and L nickel, considered as construction materials in the Alplaus heat-transfer system, were placed in the system to determine their corrosion resistance to liquid sodium and NaK. The specimens were very resistant to attack by sodium at 950 F and NaK at 850 F. There was no evidence of mass transfer between the stainless steel and nickel specimens. No transfer of mass from the hot to the cold zones occurred in one year.—NSA. 13940

### 4.7, 3.4.9, 8.4.5, 3.8.4

**The Reaction of Molten Uranium and Zirconium Alloys with Water.** (Interim Summary Report from March 15, 1955 through March 15, 1956). H. M. HIGGINS. Aerojet General Corp. U. S. Atomic Energy Comm. Pubn., AGC-AE-17 (AGC-2914-2), April 30, 1956 (Declassified January 15, 1957), 48 pp. Available from Office of Technical Services, Washington, D. C.

The molten metals uranium and aluminum and alloys of molybdenum-uranium, uranium-zirconium and Zircaloy-B were dispersed in water in order to determine if the reaction of these materials would go to completion and if the reactions were explosive in character. Test data substantiated predictions based on theory that droplet size and metal temperature were important factors in determining the extent and violence of the reactions. Zirconium-base alloys were found to react violently under certain conditions, whereas uranium and uranium alloys reacted less violently under the same conditions. Small percentages of beryllium were added to Zircaloy-B in an effort to reduce its activity. This effort was successful in that several of the resulting alloys were less reactive. (auth).—NSA. 13751

### 4.7, 6.3.6

**Solution-Rate Studies with Liquid Metals: Solution of Copper in Liquid Lead and Bismuth.** A. G. WARD AND J. W. TAYLOR. *J. Inst. Metals*, 85, No. 4, 145-152 (1956).

A study has been made of the kinetics of the dissolution of solid copper in liquid lead and bismuth under nominally static and isothermal conditions, at temperatures in the range 360-510 C. The dissolution followed an expression of the form $n_t = n_0 (1 - \exp [-(KSt)/V])$, where $n_t$ = concentration of dissolved solute at time t, $n_0$ = saturation, S = surface area of solid exposed to a liquid of volume V, and K = solution-rate constant. The solution-rate constant in the bismuth/copper system was about three times greater than that for lead/copper at any one temperature. The solution-rate constant varied with temperature thus: $K = K_0 \exp(-\Delta E/RT)$, where $\Delta E$ = the activation energy for the dissolution process. The experimental data appear consistent with dissolution being a complex process involving diffusion of solute through a laminar boundary-layer combined with convection effects introduced through d changes accompanying dissolution. From a general relationship between $(n_t/n_0)$ and $(t/t_0)$ it is possible to construct concentration/time relationships, knowing only the saturation concentration and the time to reach saturation. (auth.)—MA. 13745

### 4.7, 6.3.10

**Examination of Inconel-316 Stainless Steel-Sodium Pump Loops 4689-5 and 4689-6.** G. M. ADAMSON AND R. S. CROUSE. Oak Ridge National Lab. U. S. Atomic Energy Comm. Pubn., CF-55-6-24, June 2, 1955 (Declassified April 4, 1956), 12 pp. Available from Office of Technical Services, Washington, D. C.

The findings of a metallographic examination of the loops confirm the fact that excessive mass transfer occurs in Inconel pump loops in which sodium is circulated at 1500 F. The use of 316 stainless steel in the cold leg of the loops does not appear to increase mass transfer.—NSA. 13568

### 4.7, 8.4.5

**Problems of Liquid-Metal-Fuelled Reactors.** B. R. T. FROST. Atomic Energy Research Establishment, Harwell, Berks, England. *Nuclear Eng.*, 1, 373-377 (1956) Dec.

The problems associated with bismuth circuits are not so well understood as those involving sodium. Suggested bismuth LMFR systems are discussed with reference to mass transfer, penetration and corrosion of graphite and suitability and corrosion behavior of constructional materials. (auth).—NSA. 13580

### 4.8

**The Recent History of Corrosion in Metal Used for Internal Fixation.** W. H. CATER and J. H. HICKS. *Lancet*, 171, 871-873 (1956) October 27.

Investigation into causes of corrosion, particularly gross pitting, in stainless steel components used in pinning of fractures at Birmingham Accident Hospital. Cause was traced to substitution, by supplier, of En. 58M high-manganese 18/8 for En. 58E 18/8 steel for screws which, in contact with the En. 58E, have high corrosion rate. Substitution of 18/8 molybdenum steels or Vitallium overcame corrosive effects. Only these last 2 materials should be used, pending further investigations. Note is given on investigation into materials involved in stock of hospitals for treating fractures by pinning, disclosing extensive reserves of unsuitable materials, such as mild steel and chromium steel. Short description of suitable spot-testing techniques to differentiate suitable materials is given.—INCO. 13605

### 4.8, 5.6.3, 6.4.2

**Corrosion of Aluminum in Contact with Paper.** T. H. ANGEL. *World's Paper Trade Rev.*, 1956, 1013-1014, May 17.

Allowable chloride and water-soluble sulfate at 7% paper moisture given as 0.1% chlorine, 0.2% $SO_4$, maximum pH 5 in contact with annealed commercial-purity aluminum foil. Moisture gradent in thick paper with accumulation of moisture in contact with aluminum may cause corrosion. Surface of freshly-annealed aluminum (which is hydrophilic) becomes hydrophobic in contact with paper.—BNF. 13957

## 5. PREVENTIVE MEASURES

## 5.2 Cathodic Protection

### 5.2.2, 4.6.11

**Zinc Anodes for Use in Sea Water.** J. T. CRENNELL AND W. C. G. WHEELER. *J. Applied Chem.*, 6, Pt. 10, 415-421 (1956) Oct.

Investigation of failure of zinc anodes in sea water showed that presence of iron in excess of a few parts per million is the cause and that no other common impurity is important. While zinc of low iron content is available, difficulty is experienced in large scale production of uncontaminated anodes. Small additions of aluminum to zinc containing 200 ppm of iron produce permanently active anodes. Alloying additions refine grain size of metal and give a smooth corrosion pattern. Graphs, tables.—INCO. 13523
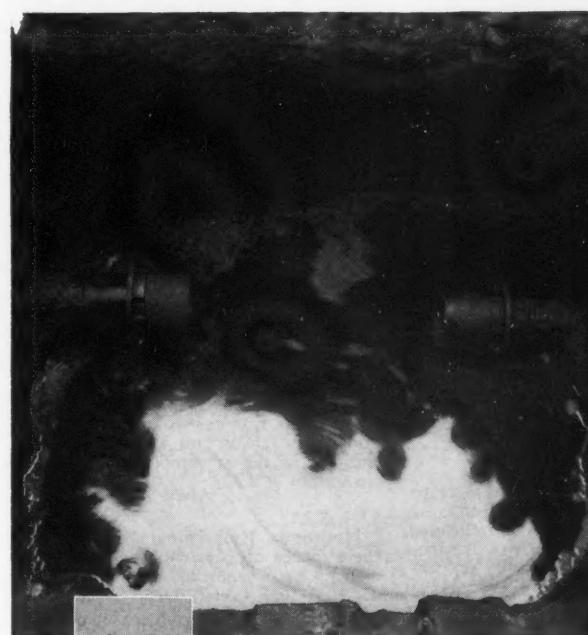
### 5.2.2, 8.9.5

**Shipboard Evaluation of Zinc Galvanic Anodes Showing the Effect of Iron, Aluminum and Cadmium on Anode Performance.** E. C. REICHARD AND T. J. LENNOX, JR. *Corrosion*, 13, No. 6, 410t-416t (1957) June.

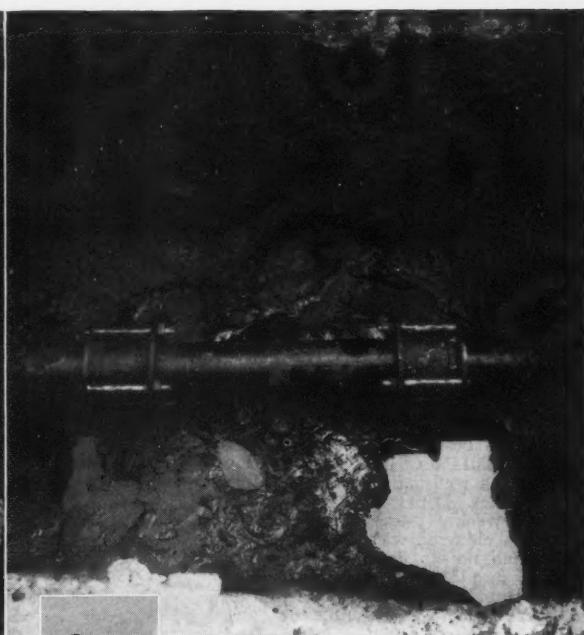A commercial zinc anode with desirable long term galvanic performance characteristics has been developed.

Aluminum plus cadmium added to zinc has produced this improved anode.

The tolerance for iron in zinc anodes has been increased by the aluminum plus cadmium addition. Less adherent corrosion products and uniform anode attrition also have been achieved without adverse effects on anode current efficiency. Improved zinc anode performance obtained with the aluminum plus cadmium addition is independent of anode current density or electrolyte temperature.

In the absence of other constituents, controlling the iron content at 0.0014 percent does not give a zinc anode with optimum galvanic properties. Best performance is obtained when the iron content is on the order of 0.0002 percent.

Barrier shields serve no useful purpose on the faying surface of zinc anodes installed on steel ship hulls.

Long term performance tests on 5 active ships and quiescent marine exposures, using commercial size zinc anodes, provide the basis for these conclusions.                                     13729

### 5.2.2, 8.9.5, 4.6.11
**Cathodic Protection of an Active Ship Using Zinc Anodes.** H. S. PREISER AND B. H. TYTELL. *J. Am. Soc. Naval Engs.,* **68,** 701-704 (1956) Nov.

The article reports a test on the effectiveness of zinc anodes, containing less than 0.0014% of iron, in protecting the hull of a well-painted tug operating in salt water. Potential readings were taken at weekly intervals and, unlike the values obtained with less pure zinc, were found not to decrease with time. After 15 months the paint film on the tug's bottom was in excellent condition and there was no corrosion. Only 20% of the zinc had been consumed and negligible amounts of corrosion products were found on the zinc anodes.—ZDA.                                     13685

### 5.2.2
**Some Considerations on the Properties of Aluminum-Zinc Alloys as a Galvanic Anode for Cathodic Protection.** (In Japanese.) M. MAEDA. *Corrosion Engineering* **6,** No. 3, 33-35 (1957) May.

Some properties of aluminum-zinc alloys as a galvanic anode for cathodic protection were considered. Aluminum-zinc alloys containing 2, 3, 4, 5, 10 and 15 wt percent zinc were tested. Microscopic structures were observed and electrode potential, corrosion rate and anodic polarization in 3% sodium chloride solution were measured. Furthermore, the corrosion rate of zinc was measured when coupled with aluminum-zinc alloys in the same solution.

Results: (1) Electrode potential becomes more negative with increasing zinc content and that of alloys containing more than 5% zinc is —0.95 V with respect to the saturated calomel electrode. (2) Corrosion rate of alloys containing less than 5% zinc is nearly equal to that of pure aluminum. (3) Aluminum-zinc alloys accelerate the corrosion of zinc when coupled together in 3% sodium chloride solution and the corrosion rate of zinc increases by a few percent in comparison with self corrosion. (4) Anodic polarization curve of aluminum-5% zinc alloy has an inflexion at the current density of 11 mA/dm².—JSPS.                           14221

### 5.2.2
**Characteristics of the Swedish Iron for Galvanic Anode on Ship Hull Protection: Technical Note. (In Japanese.)**

YUKIO SAKAE and KICHIRO ONIMURA. *J. Electrochem. Soc., Japan,* **25,** No. 4, 214-217 (1957) April.

Characteristics of Swedish iron (or low carbon steel) as galvanic anodes for ship hull protection, such as electrode potential in 3% sodium chloride solution, anode currents and polarization characteristics in contact with mild steel and corrosion resistance, etc., were studied.

Anode materials employed in the experiments are 99.9% up zinc anode, 98.5% up zinc anode, Swedish iron straps (C 0.02% and 0.04%, aluminized low carbon steel and aluminum anode.

Results: (1) Electrode potential (referred to 3.3N calomel electrode) in 3% sodium chloride solution has been measured —0.6 volt (Swedish iron straps) —0.93 ~ —1.0 volt (aluminized steel), —1.10 ~ —1.15 volt (various zinc anodes) and —0.54 ~ —0.58 volt (mild steel), so Swedish iron straps were slightly less noble than mild steel. (2) Corrosion loss of Swedish iron straps was nearly equal to that of the mild steel plate. (3) Polarization characteristics were not considered accurately as anodic polarization. (4) Aluminized steel or aluminum anodes were inadequate as galvanic anodes, because the polarized potentials were often more noble than those of mild steel in sea water or in sodium chloride solution. Therefore, the protective effects were considered very unreliable.

It is concluded that Swedish iron straps are not suitable as ship hull protectors as compared with zinc anodes. So the use of high purity zinc protectors for cathodic protection of ship hulls is preferred.—JSPS.                           14203

### 5.2.3, 8.9.3
**Cathodic Protection of a Semi-Marine Pipeline System.** B. J. WHITLEY, JR. *Corrosion,* **13,** No. 8, 117-118 (1957) August.

Methods of applying cathodic protection systems and steps taken to polarize a three-pipeline system of 10, 12 and 6-inch lines in salt water and marsh land are described.                           14200

## 5.3 Metallic Coatings

### 5.3.4
**Developments in Tin and Tin Alloy Plating, 1946-1956.** J. W. PRICE. *Product Finishing,* **9,** No. 7, 135-142 (1956) July.

Alkaline solutions; deposition of alloys of tin with lead, copper, zinc, nickel and cadmium. 33 references.—BNF.
                                     13328

### 5.3.4
**Reactions Between Chromium Chlorides and Iron at High Temperatures.** (In Russian.) N. G. KLYUCHNIKOV. *J. Applied Chem., USSR* (Zhur. Priklad. Khim.), **29,** No. 2, 161-165 (1956).

Klyuchnikov has previously shown [*Doklady Akad. Nauk. USSR,* **74,** 267 (1950)] that the chromium taking part in the chromizing process is always present only in the divalent state; confirmation of this has also been obtained by heating powdered chromium with chromic chloride in a quartz ampoule at 900 C for two hours; chromous chloride was formed. On heating iron powder with chromic chloride a similar reaction took place, iron-chromium and chromous chloride being formed; evidently the reaction $CrCl_3 + Fe = FeCl_3 + Cr$ does not occur during chromizing. Indeed in chromic chloride vapor iron is corroded

and not coated with chromium; at 650-850 C the reaction $2CrCl_3 + Fe = FeCl_2 + 2CrCl_2$ takes place and it is only at higher temperatures that the corroded specimens become coated with chromium. Chromizing with chromous chloride proceeds satisfactorily only if oxygen and water vapor are completely absent; oxygen reacts with chromous chloride to give chromic oxide and chlorine, which corrodes the work. If chromizing were to be attributed solely to the reaction $CrCl_2 + Fe = FeCl_2 + Cr$, the difference in at. wt. of chromium and iron would result in the specimens losing weight during chromizing; in practice there is an increase in weight. This must result from another reaction in which chromium is spontaneously deposited without replacing iron atoms. This behavior was particularly marked in chromizing specimens previously coated with electrolytic iron or electrolytic chromium and can thus be explained by reaction with adsorbed hydrogen. When chromizing occurs by exchange of chromium and iron atoms, the dimensions of the specimens remain almost constant, but when chromium is added without exchange the dimensions increase. Experiments on the long-time chromizing of small iron plates. ~0.15-0.20 mm. thick, using iron-chromium, showed that the process was essentially an equalization of the chromium and iron concentrations in the specimen and the iron-chromium.—MA.                           13248

### 5.3.4, 3.2.2
**Hydrogen Embrittlement in Steel in the Process of Electroplating.** (In Swedish.) Uno Trägardh. *Teknisk Tidskrift,* **86,** 1051-1057 (1956) Dec. 4.

Cathodic removal of grease; pickling; and electrolytic precipitation of zinc, cadmium, copper, tin and silver. Special notice given to the influence of hydrogen absorption on the steel.—MR.
                                     13720

## 5.4 Non-Metallic Coatings and Paints

### 5.4.5, 3.8.4
**Fundamental Studies on the Adhesion of Organic Materials to Metal Substrates.** R. L. PATRICK AND. W. A. VAUGHAN. Quantum Inc. U. S. Wright Air Development Center, Tech. Rept. 56-663, December, 1956, 86 pp.

The controlling factors which influence the bonding of adhesives and protective coatings to metal surfaces were investigated. Model systems were prepared in order to examine the phenomenon of adhesion. Single interface models were prepared by depositing monolayers on suitable metal substrates. Weight is added as bulk polymer and is polymerized directly onto the monolayer forming C-C bonds. The samples are ruptured in a modified ultracentrifuge and rupture-stress values are obtained. The results approximate pure tension values. By proper selection of substrates, it is possible to examine the monolayer prior to rupture testing. An ellipsometer is utilized for this procedure. Following rupture testing, the monolayer is again examined to determine whether or not the monolayer in the interface is removed from the metal substrate. In no case has the monolayer been removed. Values from 0.1 to several times the original monolayer thickness have been observed. (auth.)—NSA.         14011

**5.4.5, 3.8.4**

**New Aspects of Polymer-to-Metal Bonding.** N. STUART. *Plastics*, **21**, No. 230, 308-311, 313 (1956).

If copper or brass is held in contact with sulfurous material, a film of sulfide is formed at a speed which varies from point to point according to the orientation of the microcrystals. Experiments are described in which rubber is vulcanized in contact with brass and pulled off. The sulfide film adheres to the rubber, leaving the brass clean. The film is then examined by interference microscopy, revealing a mosaic structure of varying thickness. If a sulfide film is formed on a similar brass surface and a piece of adhesive cellulose tape is applied and pulled off, it is found that some sections of the mosaic are removed while others are left behind. Also, it is well known that two pieces of brass differently prepared (e.g., annealed or electro-deposited) will be indistinguishable by chemical or X-ray examination, but can have quite different properties of adhesion to rubber. It follows that the adhesion between a sulfide film and a single brass crystal depends critically on the orientation of the exposed crystal surface. The possibility is suggested that certain polymers, which at present will not adhere to metals, might in certain cases be made adhesive by the addition of a small percentage of sulfur, to produce a bonding layer at the interface.—RPI.     13921

**5.4.5, 5.9.2**

**Use of the Radioactive Tracer Technique in Aircraft Paints.** A. L. GLASS AND M. S. PELLEGRINI. *Official Digest Federation Paint and Varnish Production Clubs*, **29**, No. 384, 49-55 (1957) Jan.

By a radioactive tracer technique using $C^{14}$ it was shown that a monomolecular layer of stearic acid is not left behind after weathered paint films are stripped and the metal cleaned by procedures recommended for naval aircraft, i.e., U. S. Specifications MIL-R-8633 (Aer) and MIL-C-6135 (Aer). The presence of aluminum stearate in a zinc chrome primer originally used had no effect on the adhesion of the subsequently applied paint system. The recommended paint stripper and cleaning procedure had no effect on the adhesion of the re-coat paint system. The inclusion of a wash primer before the zinc chrome primer improves the adhesion of the re-coat system.—RPI.     14275

**5.4.5, 6.6.8**

**Epoxide Resins in Industrial Painting and Structural Protection.** *Corrosion Prevention & Control*, **4**, No. 3, (1957) March.

Papers include: 'Epikote Resin Based Coatings: A General Review', D. H. Nicholson, 'Epoxide Resin Based Finishes for the Protection of Alkaline Building Materials', H. R. Touchin, 'The Use of Epoxide Resin Based Coatings for Corrosion Prevention in a Chemical Refinery', J. L. Francis, 'Epoxide Resin Based Cements', 'The Economies of Painting', R. N. Wheeler, 'The Protection of Structural Concrete', P. B. Cormac.—INCO.     14116

**5.4.5, 8.9.3, 2.3.7**

**Tentative Recommended Specifications for Asphalt Type Protective Coatings for Underground Pipe Lines: Mastic Systems. Second Interim Report. NACE Technical Unit Committee T-2H**

on Asphalt Type Pipe Coatings (A. S. Joy, Chairman). *Corrosion*, 13, No. 5, 347t-350t (1957) May.

Asphalt-type mastic systems for application to underground pipe lines are described, materials characteristics specified and application methods and minimum satisfactory coatings indicated. Included among the recommendations are surface preparation criteria, priming methods, electrical inspection, pipe handling methods and maintenance. An appendix details methods for testing both bond strength for primers and pipe line coatings themselves. 13844

## 5.6 Packaging

### 5.6.1
Prevention of Corrosion in Packaging and Storage. The Selection of the Packaging Method. F. A. PAINE. Paper before Soc. Chem. Ind., Symposium on Prevention of Corrosion in Packaging and Storage, Birmingham, April 11-12, 1956. *Chemistry and Industry*, No. 10, 288-291 (1957) March 9.

Discussion of factors which influence selection of packaging method for a metal item. Item should be designed to achieve best compromise between production and packaging and should be clean and free from contamination of all kinds before application of protective. Method of protection employed should be selected after taking into account sensitivity of item to corrosion, climatic and other hazards likely to be met during transit and length of period elapsing between packing and use. Packaging materials in immediate contact with packed item should be free from corrosive substances and permissible amounts of these should be specified. Diagrams. —INCO. 13849

### 5.6.1
Prevention and Corrosion in Packaging and Storage: The Control of Atmospheric Corrosion of Metals in Storage and Transit. E. L. EVANS and E. G. STROUD. Paper before Soc. Chem. Ind., Symp. on Prevention of Corrosion in Packaging and Storage, Birmingham, April 11-12, 1956. *Chemistry & Industry*, No. 9, 242-248 (1957) March 2.

In considering factors controlling atmospheric corrosion, formation of primary oxide film, critical humidity, breakdown of primary oxide film at primary critical humidity and acceleration of corrosion at secondary critical humidity and promotion of corrosion by solid particles (corrosion products and contaminants) are discussed. Many references are made to corrosion of steel in sulfur dioxide and effect of humidity as determined by Vernon and by Skorchelletti and Tukachinskii. Peculiar conditions leading to corrosion of metals in storage and in packages, such as contaminants within package and condensation, are reviewed. Corrosion preventive measures include maintenance of cleanliness in factory, use of impervious wrappings and protective coatings, reduction of humidity, elimination of volatile contaminants and use of contact and volatile corrosion inhibitors. 29 references.—INCO. 14081

## 5.9 Surface Treatment

Relationship Between the Anode Potential of Steel and the Composition of the Electrolyte in Electrochemical Polishing. N. P. FEDOT'EV AND S. YA. GRIL-

IKHES. *J. Applied Chem.*, USSR (Zhur. Priklad. Khim.), 30, No. 2, 233-239 (1957).

Anode potential as a function of current density is investigated for electrolytes containing phosphoric acid, sulfuric acid and chromium trioxide at various temperatures and electrolyte compositions. 6 figures, 4 references.— ATS. Translation available: Associated Technical Services, P. O. Box 271, East Orange, New Jersey. 13778

### 5.9.4, 6.3.6, 6.3.10
Surface Condition and Anode Potentials of Copper and Nickel in Electrochemical Polishing. N. P. FEDOT'EV and S. YA. GRILIKHES. *J. Applied Chem.* USSR (Zhur. Priklad. Khim.), 30, No. 4, 643-645 (1957).

Experiment revealed the formation of passive oxide films. 1 table, 3 figures, 4 references.—ATS. Translation available: Associated Technical Services, P. O. Box 271, East Orange, New Jersey. 14304

### 5.9.4, 6.3.13, 3.5.4
Effect of Ultraviolet Irradiation on the Growth of Anodic $Ta_2O_5$ Films. D. A. VERMILYEA. *J. Electrochem. Soc.*, 104, 212-217 (1957) April.

Ultraviolet irradiation during the growth of amorphous tantalum oxide films in aqueous solutions results in the transformation of the outer portion of the film from tantalum oxide to a material which dissolves more rapidly than tantalum oxide in hydrogen fluoride. If the formation field is high, the transformed region has a very high resistance and both tantalum and oxygen are mobile in the region. When the formation field is low, the region has a lower resistance, contains water which can be removed partially by heating the film in air and only oxygen is mobile. —MR. 14124

### 5.9.4, 6.4.2
Pseudo-Subgrain Structures on Aluminium Surfaces. N. C. WELSH. *J. Inst. Metals*, 85, Pt. 4, 129-135 (1956) Dec.

A number of workers have reported periodic markings of spacing about $0.1\mu$ on the surface of electropolished aluminum and its alloys. The present investigation was made to explore the possibility that the markings represent some regular incoherence in the grain structure of the metal. High-purity annealed aluminum was electrolyzed under conditions ranging from electropolishing to heavy anodic oxidation. Electron microscopy showed, in some cases, regular markings of diverse pattern and of spacing $0.03$-$0.3\mu$. The patterns varied according to the electrolyte, the conditions of electrolysis and the crystallography of the metal surface. In all cases the dominant factor controlling the surface morphology was the potential applied to the electrolyte cell. The spacing of the markings increased progressively as the potential increased, the upper limit being set by breakdown of the anodic barrier layer. The changes of pattern and spacing and their dependence on the electric field are incompatible with the concept of a subgrain structure. The postulate is made that the markings originate from a micro-etch process acting through, and controlled by, a disperse anodic film. (auth)—ALL. 14025

### 5.9.4,-6.4.4
Surface Availability of Inhibitors in Protective Coating Systems. Pt. I. Dichromate Treatment of Magnesium Surfaces. MAX KRONSTEIN and JOSEPH C.

PETTORINO. *Paint and Varnish Production*, 46, No. 12, 36-41 (1956) November.

In the corrosion protection of metals it has been established that certain groups, such as chromate matter, have a delaying effect on the progress of corrosion. This paper is concerned with the effect of dichromate sealer treatments on pre-pickled FS-1 magnesium and shows that panels with this treatment and one subsequent coat of an organic coating resist the corrosive exposure in the saltfog chamber longer than without this treatment. The effect of the treatment is dependent also on the pH of the treating solution.

That the treatment actually produces a chromium-based coating is shown by the X-ray spectrograph. That the coating is capable of releasing soluble matter is shown by pH measurements in distilled water in which these surfaces have been immersed for certain time intervals. The matter which enters the water solution, reacts with materials which are capable of forming colored chromate derivates and the progress of this chromate formation can be measured by colorimetric methods.

The rate of the release of this soluble matter can be delayed by the application of a protective film of a clear lacquer before the water immersion of the treated surfaces. —(auth). 14101

### 5.9.4
The Control of Anodic Oxide Coatings Using the ISML Resistometer. (In Italian.) A. PRATI. *Alluminio*, 25, No. 9, 385-388 (1956) Sept.

Using the ISML Resistometer author has studied the effect of alloy composition on the breakdown voltage of the anodic coating. Suggests working limits for use in inspection procedure.—BNF. 13306

## 6. MATERIALS OF CONSTRUCTION

## 6.2 Ferrous Metals and Alloys

### 6.2.3, 1.6, 5.4.5
Protective Painting of Structural Steel. F. FANCUTT AND J. C. HUDSON. Book, 1957, 102 pp. The MacMillan Company, 60 Fifth Ave., New York 11, N.Y.
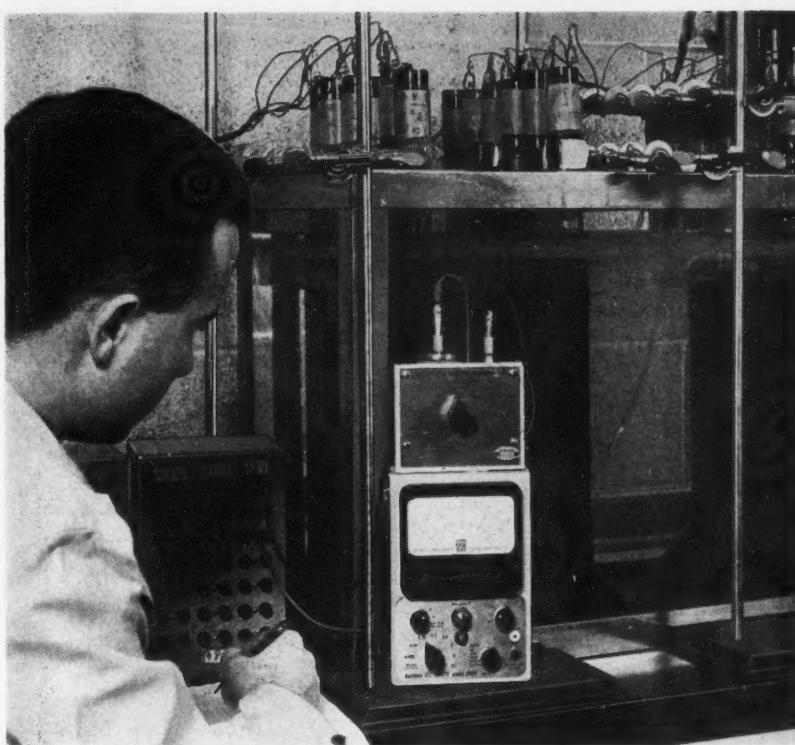
A summary of British practice for protection of steel from atmospheric corrosion, essentially a revision and expansion of an earlier work (Protective Painting of Structural Steel, Publ. 1941) prepared and published by the Protective Coatings (Corrosion) Sub-Committee of the British Iron and Steel Research Association.

Contents include principles, surface preparation, choice of systems for new steel work, procedure, repainting of old steelwork, practical examples and special cases. Appendices cover some formulations and particulars regarding test sites. There is an alphabetical subject index. 13756

### 6.2.3, 3.5.9, 3.2.2
Effect of Temperature on the Fracturing Behavior of Mild Steel. J. D. LUBAHN. Gen. Elec. Co. *Welding J.*, 35, No. 11, 557s-568s (1956) Nov.

Fracture properties observed at various temperatures in 4-inch SAE 1020 steel plate were: strength, energy-absorbing capacity, ductility (local plastic strain preceding crack initiation) and amount of gradual tearing preceding brittle crack propagation by cleavage.

Each property was measured for various temperatures, loading rates and biaxialities for both notched and unnotched specimens cut in both rolled and thickness direction of plate. Above +150 C ductility, strength and energy-absorbing capacity are large and crack propagates by gradual fibrous tearing. Fibrous fracture disappears at +30 to —40 C and energy values are low. Ductility becomes very small at —100 to —180 C. Slow notch bend strength rises continuously with decreasing temperature to —150 C and then drops slightly. Below —80 C, complete separation occurs when first crack appears. Notch bend ductility is same as biaxial unnotched bend ductility at room temperature, but much less at —60 C to —120 C. Ductility in normal direction is lower and more erratic than in rolling direction, but strengths are same except below —150 C. Transition temperature in Charpy impact test is related to temperature range where metal is losing ability to tear, while transition temperature in unnotched impact bend test is related to temperature where metal is losing its ductility. Tables and graphs present data down to —200 C. 33 references.—INCO. 13687

### 6.2.4, 3.7.2
**Effect of Nickel and Chromium Contents on the Weldability of High Tensile Manganese-Silicon Steels. Rept. 1.** H. KIHARA, H. SUZUKI, H. TAMURA, T. ODA, K. MIYANO and K. TAZIMA. Paper before Japan Welding Soc., Fall Mtg., 1955. *J. Japan Welding Soc.*, **25**, No. 12, 688-695 (1956) Dec.; *Library Abst. Bull.*, Japan, No. 3, VI-6 (1956) July-Dec.

Fourteen experimental metals containing 0.06-0.93 nickel and 0.03-0.91 chromium were added to 14 batches of the base metal containing 0.16 carbon, 1.10 manganese and 0.45 silicon melted with high frequency induction furnace. Samples were rolled into 20 mm plates to be tested. Four commercial heats were made also in basic open hearth furnace and rolled into the same form and compared. For testing weldability, tensile, V-Charpy impact, weld-maximum

hardness, Jominy, Kommerell, Kinzel, slit-type cracking, CTS cracking, gas cut bend and fillet weld break tests were used. Tensile strength increases at a rate of 3 kg/mm² with 1 nickel increase both in as rolled and normalized conditions, and at 3 kg/mm² in as rolled condition and 6 kg/mm² in as normalized condition with 1 chromium increase. Nickel increases the yield strength at 4-5 kg/mm² per 1% of its increase while chromium showed no effect on yield strength. Energy transition temperature in V-Charpy test is lowered by nickel but raised by chromium. Effect of nickel or chromium on tensile and yield strengths is very little when the content of nickel or chromium is limited under 0.25 and 0.10% respectively. However, the 15 ft-lb transition temperature seems to be lowered slightly and elongation increases appreciably when nickel and chromium contents are reduced extremely, while the energy or shear fracture transition temperature appears unaffected.—INCO. 13652

### 6.2.4, 3.7.3
**Welding Test on Heat Resisting Chromium-Molybdenum Steel. Rept. I.** T. KAWAMURA, I. OKAMOTO, S. HAMADA and Y. FUKUZONO. Paper before Japan Welding Soc., Fall Mtg., 1955. *J. Japan Welding Soc.*, **27**, No. 7, 386-391 (1956) July; *Library Abst. Bull.*, Japan, No. 3, VI-4 (1956) July-December.

Various tests on welding of 4-6 chromium-½ molybdenum and 9 chromium-1 molybdenum steels were conducted. Since chromium-molybdenum steels are extremely self-hardenable, it is necessary to preheat the steels at 400-600 F before subjected to welding and maintain same temperature during entire welding process. When welded with austenitic stainless steel electrodes semi-soft annealing is best, but with suitable electrodes of compatible composition, full annealing is recommended. Austenitic stainless steel electrodes are inferior to the electrodes of compatible composition in hardness, mechanical properties and micro-structure except in weldabil-

ity. Occurrence of ferrite band was observed after heat treatment when the austenitic stainless steel electrode was used.—INCO. 13615

### 6.2.4, 3.7.3
**Welding Test on Heat Resisting Chromium-Molybdenum Steel. Rept. II.** T. KAWAMURA, I. OKAMOTO, S. HAMADA and Y. FUKUZONO. Paper before Japan Welding Soc., Fall Mtg., 1955. *J. Japan Welding Soc.*, **27**, No. 8, 433-437 (1956) August; *Library Abst. Bull.*, Japan, No. 3, VI-5 (1956) July-December.

To investigate boundary defects of these steels, authors tested high temperature tensile strength, temperature of ferrite band formation and corrosion resistance of the steels. In high temperature tension test of 4-6 chromium-½ molybdenum steel welded with austenitic stainless steel electrodes, the breakdown was observed at the weld metal in its welded condition but when it was semi-annealed the breakdown occurred at the base metal. In the 9 chromium-1 molybdenum steel, the breakdown occurred at the base metal with any kind of electrode used or any kind of heat treatment applied. Ferrite band defect formed by heat treatment was observed in the room temperature test but not in the high temperature test. Formation of this band began at 500 C and the growth was made above that temperature. Corrosion resistance of the ferrite band was poor and corroded in boiling 5% sulfuric acid in 10 hours. It corroded even in as-welded condition.—INCO. 13647

### 6.2.4
**Properties and Weldability of High-Strength Pressure-Vessel Steels in Heavy Sections.** J. H. GROSS AND R. D. STOUT. Paper before American Welding Society, Nat'l Fall Mtg., Cleveland, October 8-12, 1956. *Welding J.*, **36**, No. 3, 157s-167s (1957) March.

Study of effects of plate thickness and of position in plate on mechanical properties and weldability of high-strength pressure vessel steels. Steels chosen for testing were A201 Grade A, A302 Grade B, Navy G (2.16-2.58 nickel) and T-1 (0.84-0.87 nickel). Testing schedule permitted comparison of properties between 1-inch plates and 4-inch plates and between locations with respect to width and thickness dimension of 4-inch plate. Tables give results of tension tests for yield strength, tensile strength, elongation and reduction of area; V-notch Charpy tests of base metal for ductility and fracture transition; cantilever beam fatigue tests for allowable strain range for 100,000 cycle fatigue life; Kinzel tests for transition temperature; and longitudinal bead-weld underbead cracking tests. Tables, photomicrographs.—INCO. 14161

## 6.3 Non-Ferrous Metals and Alloys—Heavy

### 6.3.6, 8.9.5
**Investigation of Properties and Uses of Aluminum Bronzes for Shipboard Applications: A Summary of Work Completed Through Sept. 1955.** W. L. WILLIAMS. U. S. Naval Eng. Experiment Station, Rept. No. 040037B(22), NS-013-118, Feb. 1, 1956, 125 pp.

Summary of all work conducted by Station's Metallurgical Laboratory to evaluate various cast and wrought aluminum bronzes for shipboard service. Experiments included variety of sea water and fresh water corrosion tests (corrosion-erosion, partial immersion, velocity,

jet impingement, hydraulic cavitation, stress-corrosion) on plain and welded alloys, as well as tension, torsion, fatigue, corrosion fatigue and magnetic permeability tests. Experiments, often of simulated service type, were conducted to evaluate alloys for specific applications such as condensers, salt water piping, salt water pumps, reduction gears, bolts, propulsion shafting, shaft sleeves, propellers, valve trim and fresh

water stills. Bronzes studied contained up to 15 aluminum with additions of nickel, iron and silicon. Data are given for 90-10 and 70-30 copper-nickel alloys for comparison (90-10 in condenser applications in particular). Numerous tables, graphs, corrosion specimen photographs.—INCO.　　　14027

**6.3.8**

**The Properties of Tellurum-Alloy**

**Lead Sheath for Power Cable.** H. A. HOOVER. Paper before Am. Inst. Elec. Engrs., Fall General Mtg., Chicago, Oct. 1-5, 1956. *Trans. AIEE*, 75, Pt. III, 1517-1521; disc., 1521-1525 (1957) Feb.

Tellurium-alloy lead possesses excellent resistance to creep and bending fatigue and is greatly superior to copperbearing lead in these respects. It may be extruded over a wide range of extrusion temperatures and foundry prac-

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tices without significantly affecting properties of finished product. Only a slight age-hardening trend is evident after prolonged aging at room temperatures. Ductility remains high after 5½ years aging. Bending life of alloy remains unaffected by exposure to heat equivalent to that received in wiping operations. Under conditions of electrolytic corrosion and direct chemical attack, corrosion resistance of tellurium-alloy lead shows some superiority over corrosion resistance of copper-bearing lead. Photomicrographs, graphs, photos, 18 references.—INCO. 14295
6.3.8

**On the Corrosion-Proof, Mechanical Properties and Microstructure of Lead and Lead Alloys.** M. HANAFUSA and R. KAWABATA. *J. Japan Inst. Metals,* **21,** No. 1, 35-43 (1957) January.

Some chemical, mechanical and microstructural experiments on lead and lead-antimony alloys as materials for apparatus in the chemical industry have been carried out. (1) At temperature range of 50-80 degrees, the greater the antimony content the better is the resistance to sulfuric acid. (2) With tellurium and copper alloying, the flash point of lead-rich alloys rises, but with bismuth, zinc, tin, and antimony it is lowered. (3) As the lamella $\beta$ phase appears in grain structure, the tensile strength of the rolled lead is lower than one cast, both having the same content of lead-antimony alloy. (4) Relation between the microstructure and the flash point on lead and lead rich alloys is explained.—JSPS. 14285

6.3.9, 1.6
**Molybdenum.** L. NORTHCOTT. Book, 1956, 222 pp. Butterworths Scientific Publications, London; Academic Press, Inc., New York.

Until recently, the main use of molybdenum has been as an alloying element in steel; its use as a pure metal has been small, chiefly in lamps and radio valves and as windings in high-temperature furnaces. However, since engine designers are asking for materials with high strength at ever-increasing temperatures, a great deal of research has been put into developing molybdenum-base alloys as high-temperature engineering materials. The high melting point of molybdenum and its not unreasonable specific gravity of 10.2 suggest that such research work is well worth while. The results of this work have been very adequately summarized by Dr. Northcott in the latest book of the series "The Metallurgy of the Rarer Metals". He deals with extraction, physical and mechanical properties, powder metallurgy, arc-melting, fabrication, alloys, welding, and protection of molybdenum against oxidation. Dr. Northcott's book will be essential to anyone undertaking research on molybdenum and very useful to anyone who has occasional dealings with the metal.

There is a very important omission, which the reviewer regrets, viz. a short chapter, such as Dr. Sully gives in his book on "Chromium" in the same series, summarizing the prospects for molybdenum as a high-temperature engineering material. For such applications, molybdenum is a very exasperating metal. Very high creep strengths have been obtained in certain alloys. Dr. Northcott quoted 100-hour stress rupture strengths of over 11 tons per square inch at 1093C. Further, these high strengths are combined with ductility at room temperature; provided that the test-pieces are pulled slowly in a warm room and are free from notches, reductions in area at fracture of 60% can be obtained. Nevertheless, molybdenum-base alloys at the moment cannot be used in gas turbines, since they oxidize strongly at temperatures over 700C and neither an inherently oxidation resistant alloy nor a self healing coating has been developed. The development of an inherently oxidation-resistant alloy is very difficult, since small additions of alloying elements tend to embrittle molybdenum and yet even large additions of alloy such as 15% of nickel do not give useful oxidation resistance. Useful lives at temperatures of over 1000C have been obtained with coated molybdenum, but any flaw quickly leads to failure. Further, the best of the coatings are brittle and this brittleness and the lack of self-healing qualities rule out coated components for application such as aeroplane gas turbines, where reliability is essential. However, a great deal of work is being put into the investigation of molybdenum and it is very possible that a solution to the coating problem will be found, thus enabling the very good creep properties of molybdenum to be utilized.—MA. 13960

6.3.9, 3.7.3
**Investigation of the Effects of Hot-Cold Work on the Properties of Molybdenum Alloys.** M. SEMCHYSHEN and R. Q. BARR. Climax Molybdenum Company of Michigan. U. S. Wright Air Development Center Pubn., Jan., 1957, 126 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington, D. C. (Order PB 121976.)

Among the results of this investigation, it was shown that molybdenum alloyed with 0.28% niobium or with 0.50% titanium was strain hardened when rolled or forged at temperatures up to 2400F. Tests showed that the hardness produced by a given amount of deformation varied with the temperature at which such deformation was accomplished. In general, deformation accomplished by forging developed higher strain hardening than deformation by rolling. At the highest forging temperature of 2400F, specimens from the niobium alloy were less severely strain hardened than comparable specimens from the titanium alloy, owing to the relatively greater structural stability of the latter. The higher the working temperature in the range 1800-2400 F, the higher the hardness of the wrought structure, provided no recrystallization occurred. This anomaly suggested that strain-aging occurs during the hot-cold working of these alloys. The hardness resulting from hot-cold working by forging or by rolling could only qualitatively be related to annealing times and temperatures necessary to bring about softening. It was concluded that stress had an accelerating effect on the recrystallization of the alloys investigated. 14165

6.3.9, 5.3.2, 3.5.9
**Molybdenum for High Strength at High Temperatures.** R. R. FREEMAN AND J. Z. BRIGGS. Paper before Am. Rocket Soc., 11th Ann. Mtg., N. Y., Nov. 26-29, 1956. *Jet Propulsion,* **27,** No. 2, Pt. 1,

138-147 (1957) Feb.; *Machine Design,* **29,** No. 4, 137-138, 140, 142, 144 (1957) Feb. 21.

Stress rupture strength and 2nd-stage creep rate data at 1600, 1800 and 2000 F (shown in graphs) for molybdenum and 3 molybdenum-base alloys (0.3 niobium-molybdenum, 0.5 titanium-molybdenum and 1.0 vanadium-molybdenum) show that mechanically-worked and stress-relieved 0.5 titanium-molybdenum has best high temperature properties. Room and elevated temperature tensile properties of 0.5 titanium-molybdenum alloy are tabulated. Importance of adequate protective coatings is considered. Table evaluates sprayed coatings, including nickel-chromium-boron + aluminum-chromium-silicon and electroplated chromium + nickel coating, with respect to oxidation at 1800 and 2000 F, ballistic impact and

erosion at 1800 F. Fabrication and joining methods are discussed. Various applications of molybdenum in jet propulsion field are considered. Factors making it a logical choice include high creep and rupture stress, high tensile strength at high temperatures, high modulus of elasticity, high thermal conductivity coupled with low specific heat and low expansivity, high resistance to erosion by hot gases and high melting point. Table compares compression creep properties of swaged molybdenum with those of S-816, Nimonic 90, Stellite 21 and Metamic LT-1. Erosion specimens of sintered molybdenum, unalloyed arc-cast molybdenum, Stellite No. 6, Carpenter Red Tough tool steel and 1020 cold rolled steel, after exposure to high speed, high pressure gases at 2500-3000 F are shown.—INCO. 13747

## 6.3.10

**The Development of Alloys Containing Mainly Nickel and Chromium in Use at High Temperature.** W. BETTERIDGE AND A. W. FRANKLIN. Paper before Journees Metallurgiques d'Automne de la Soc. Francaise de Metallurgie, Paris, Oct. 28, 1954. *Rev. Met.,* **53,** No. 4, 271-284 (1956) April; *Metal Treatment & Drop Forging,* **23,** Nos. 132, 133, 343-348, 385-389 (1956) Sept., Oct.

Betteridge and Franklin review the creep, fracture, fatigue, and resistance to oxidation and corrosion of the nickel-chromium-titanium-aluminum (Nimonic) alloys between 750 and 1000 C and discuss the influence of composition and heat-treatment on their structure. They show that the progressive improvement on the nickel-chromium matrix resulting from hardening by precipitation with titanium and aluminum has led to an increase in the resistance to creep and fracture at elevated temperatures. This is shown by the fact that Nimonic 80, introduced in 1941, was fractured in 100 hours under a stress of 20 kg./mm.$^2$ at 720 C, while the most recent member of the series, Nimonic 100, fractures in 100 hours at the same stress at 860 C. There is a corresponding improvement in the resistance to fatigue and in the short-time tensile and torsion properties at elevated temperatures.—MA. 13513

## 6.3.15

**Development of a Heat-Treatable Titanium Alloy Having Adequate Formability.** H. A. ROBINSON and others. Battelle Memorial Institute. U. S. Wright Air Development Center Pubn., Jan., 1957, 78 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington, D. C. (Order PB 121942.)

This research was directed toward the development of an alloy capable of being solution heat-treated, formed in the soft as-quenched condition and subsequently reheated or aged at moderate temperatures to a condition of high strength. A series of 27 experimental alpha-beta titanium alloys was melted, forged, rolled to sheet and evaluated by true stress-true strain tensile data and bend tests. In general, the solution temperature had greater effect than alloy composition on the relative formability of the alloys in the as-quenched condition. However, several compositions appeared to offer greater promise than the others from the standpoints of formability and ability to be aged to a high strength level. A titanium-3 iron-3 molybdenum-2 aluminum alloy was particularly promising. 14135

## 6.3.15

**The Relative Corrosion Resistance of Titanium and Some of Its Alloys.** L. B. GOLDEN, W. L. ACHERMAN and D. SCHLAIN. U. S. Dept. Interior, Bur. Mines, Rept. of Investigations No. 5299, January, 1957, 25 pp.

Titanium-manganese, titanium-chromium-iron and titanium-vanadium-iron alloys with 2 types of unalloyed titanium (arc melted and sintered powder) were tested in sulfuric acid, phosphoric acid, hydrochloric acid, nitric acid and mixed acids and in various chloride solutions. Tests were carried out at 35, 60 and 100 C with air saturation and at boiling point without aeration. Arc-melted titanium is slightly superior to titanium consolidated by powder metal-

# Inco high-temperature research note:

# Effect on heat resistant alloys of the combustion products of Bunker "C" fuel oil

The use of Bunker "C" and other types of residual fuel oils for industrial heating poses a severe high temperature corrosion problem.

Combustion products from these fuels include a considerable amount of ash containing vanadium pentoxide, sodium and sulfur compounds, which have a low fusion temperature.

When this ash is liquid, it creates a fluxing action on the metals and high corrosion rates follow.

Since long field experience has shown all of the heat resistant alloy to be susceptible to this type of damage, an approach based on the addition of substances to the fuel oil to prevent the ash from becoming molten has been adopted.

### Inco High Temperature Engineering Service conducts in-plant tests

Inco engineers—in cooperation with several Steam Power and Stationary Gas Turbine com-
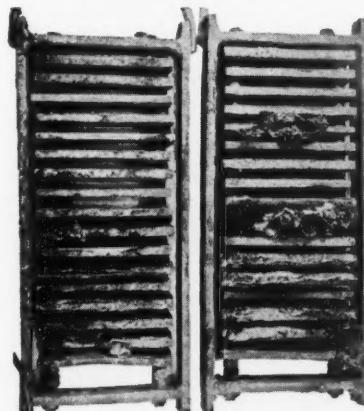
**Test racks after exposure**

Each rack carried many specimens of different compositions, all precisely measured before installation. Corrosion rates are developed from these specimens by metallographic examination.

panies have conducted a series of in-plant tests in order to determine the behavior of certain high temperature alloys when exposed to Bunker "C" burned with or without additives.

Corrosion results were obtained on both cast and wrought alloys as well as on some alloys with various coatings. The bar graph (below) shows the results of nine of the alloys tested. (Note for example, the performance of type 310 under the

severe vanadium, sodium and sulfur environment.)

In general, data derived from this Inco High Temperature test points up the benefits of using additives when burning Bunker "C" fuel oil. It also provides a basis for material selection in terms of cost and length of service.

Inco has investigated many metals and alloys under hundreds of high temperature environments. If you have a metal problem involving high temperature performance let us help you. Send for our High Temperature Work Sheet . . . a form that makes it easy for you to outline your problem to us.

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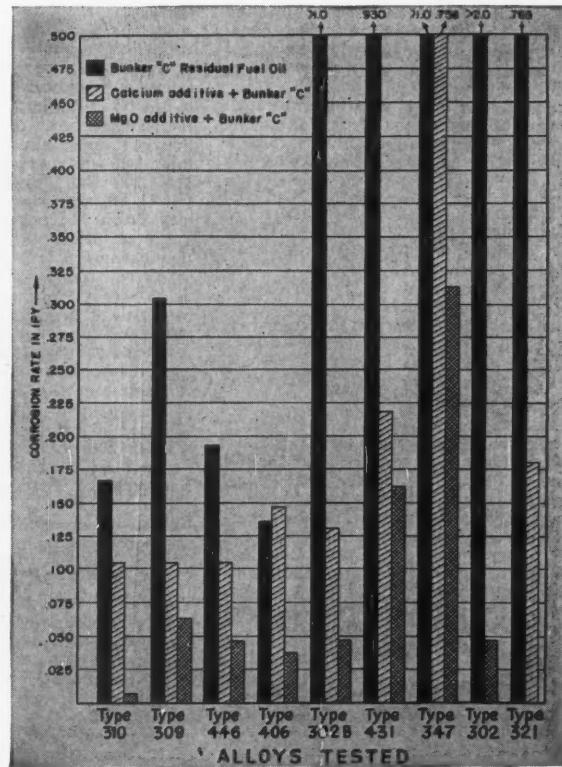
lurgy techniques in its resistance to sulfuric acid and phosphoric acid solutions. The three alloys become embrittled in more concentrated acid solutions, degree of embrittlement being proportional to corrosion rate. Study of zirconium-Titanium alloys in sulfuric acid, hydrochloric acid and phosphoric acid shows that as little as 14 zirconium is effective and that larger amounts produce progressively better resistance. Tables, graphs.—INCO.

14159

### 6.3.15, 3.7.2

**Study of Effects of Alloying Elements on the Weldability of Titanium Sheet.** J. F. RUDY and others. Armour Res. Foundation. U. S. Wright Air Development Center Pubn., March, 1957, 151 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington, D. C. (Order PB 131049.)

To 5 aluminum-titanium were introduced combinations of carbon, nitrogen, and oxygen, intended to total 0.33% interstitial. Each of the five resulting alloys was divided into three parts: one was vacuum annealed to reduce hydrogen to less than 50 ppm; the second was hydrogenated to 100 ppm; and the third was hydrogenated to 200 ppm. Each of the 15 alloy samples was then tested as fabricated, as-welded and after three separate post-weld heat treatments. A similar procedure was followed with 6 aluminum-4 vanadium-titanium alpha and beta alloy. The 5 aluminum-titanium becomes not weld ductile when the nitrogen+ogyven additions total 0.25%. This was true with 0.049% carbon and 0.123% carbon. Some ductility was indicated in both. However, the 6-inch long welded bend specimens were not able to fold to less than one-inch end distance separation without failing. Ductile welds were obtained with nitrogen+oxygen of 0.16% even with moderately high (0.28%) carbon. A completely brittle alloy was obtained when nitrogen-oxygen totalled 0.28%. The 6 aluminum-4 vanadium-titanium alloy becomes weld embrittled as carbon+nitrogen+oxygen as low as 0.26% when nitrogen is 0.11%. If the nitrogen is held lower, a carbon+nitrogen +oxygen of approximately 0.29% can be tolerated. Nitrogen appears to be a much more effective embrittler than oxygen.

14173

### 6.3.15, 3.7.3

**The Effect of Various Heat Treatment Cycles Upon the Mechanical Properties of Titanium Alloys with Various Interstitial Levels.** B. F. HADLEY, G. W. BAUER and D. EVERS. Mallory-Sharon Titanium Corp. U. S. Wright Air Development Center, March, 1957, 220 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 131009.)

The effects of various heat treatments on mechanical properties of the alloys titanium-5 aluminum complex, titanium-3 manganese complex, titanium-6 aluminum-4 vanadium, and titanium-4 aluminum-4 manganese were examined. The heat treatments were a solution treatment and age cycle, a step quench cycle, and a solution treatment, isothermal transformation cycle. The effects of interstitial levels, or interstitial element contents and sections size were also studied.—OTS.

14268

### 6.3.15, 4.3.2

**Protective Film on Titanium in Hydrochloric Acid.** RIKURO OTSUKA. J. Metals, **9**, 75-76 (1957 Jan.; *Z. Metallkunde*, **47**, No. 11, 714-715 (1956) Nov. Experiments indicate film may be a hy-

dride. Techniques are discussed which are believed to produce hydrides or to remove them prior to hydrochloric acid tests. 4 references. Cf. Otsuka: *J. Japan Inst. Metals*, **20**, No. 1, 9-11 (1956)—MR.

13904

### 6.3.15, 6.3.20, 6.3.13

**Titanium, Zirconium and Tantalum for Control of Corrosion: A Review.** WILLIAM E. LUSBY, JR. *Corrosion*, **13**, No. 10, 654t-658t (1957) Oct.

The corrosion resistant properties of tantalum, zirconium and titanium are reviewed and progress in process applications presented. Fabricating know-how and industrial experience have progressed to the point that these metals can be accepted as reliable materials of construction. Additional fundamental research is needed, however, to understand the mechanisms of attack and passivity noted. The use of these metals can now be economically justified in many locations. Volume production and lower prices forecast for titanium and zirconium due to defense needs will lead to expanded use in corrosion resistant applications.

14229

### 6.3.15

**Elevated-Temperature Fatigue-Strength of Titanium Alloys Under Axial Load (and Their Resistance to Oxidation).** GEORGES VIDAL. *Rev. Met.*, **53**, No. 10, 767-774 (1956).

Vidal studied the fatigue strength at temperatures up to 500-600 C and the resistance to oxidation of three titanium alloys manufactured in France: titanium 150A containing iron 1.3 and chromium 2.5%, MST1 containing aluminum 2.8 and copper 5.4%, and MST2 containing iron 2.0 and aluminum 1.8%. The resistance to oxidation of the three alloys was distinctly higher than that of a straight 0.35% carbon steel, lower than that of an 18:8 steel and sufficiently high for use in ordinary atmospheres at temperatures of the order of 500-550 C. The resistance to fatigue at elevated temperatures under axial load of polished specimens is appreciably higher in the range of temperatures studied than that of the Duralumin-type alloys. At 550 C the fatigue limit of MST1 is equal to that of Duralumin at ordinary temperature; but the equivalent temperature for MST2 is 500 C and for titanium 150A 450 C. In general, the elevated-temperature fatigue strength of polished specimens of these three alloys is higher than that of 0.35% carbon steel even at ~500 C., but very considerably lower at ordinary temperature. The fall in the mechanical properties of the titanium alloys occurs at a higher temperature than that of ordinary steels, but at lower temperature than that of the 18:8 stainless steels.—MA.

13731

### 6.3.15

**Basic Research on Sintered Titanium Powder Analogous to "SAP" for High Temperature Strength.** E. P. WEBER. Clevite Research Center. U. S. Navy Bureau of Aeronautics, June, 1956, 44 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington, D. C. (Order PB 121559).

Progress is reported in the development of titanium alloys by powder metallurgy which have the excellent high temperature strength and stability of SAP, or sintered aluminum powder. The sintered titanium powder was desired because of its high melting point, a shortcoming which limits the use of SAP. Procedures are described which produced a high-quality titanium hydride

with outstanding room temperature tensile properties. The base powder of an average particle size of five to 10 microns was made, compacted, dehydrided, sintered, and extruded into rod. Thorium oxide was found to be stable in titanium when sintered at 1200 C, indicating that it can serve as the dispersed phase for dispersion hardening if a fine enough dispersion can be achieved.

13721

### 6.3.15

**Stability of Commercial Alpha-Beta Titanium Alloys.** D. A. WRUCK. U. S. Wright Air Development Center Pubn., August, 1956, 35 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 121655).

The influences of various factors such as temperature, time-at-temperature, stress and hydrogen on the stability characteristics of a number of commercial alpha-beta titanium alloys was examined. Also studied was the nature of the reactions responsible for the ductility loss in unstable microstructures. Among results of the tests it was shown that in the absence of hydrogen contamination most alpha-beta alloys can be rendered quite stable up to the maximum temperatures at which they retain useful strength for stressed applications. Ductility was found to steadily reduce to a minimum at the first sign of an unstable trend and no changes are apparent with continued isothermal exposure. Application of stress tends to accelerate embrittling reactions in a microstructure with marginal thermal stability at a given temperature. The influence of hydrogen on the stability of alpha-beta alloys is dependent on the alloy composition.

13703

### 6.3.15

**Survey of Physical-Property Data for Titanium and Tiatnium Alloys.** H. W. DEEM AND C. F. LUCKS. Titanium Metallurgy Lab., Battelle Memorial Institute, March, 1956, 37 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 121613).

13590

### 6.3.15, 3.7.4, 3.7.2

**The Effect of Microstructural Variables and Interstitial Elements on the Fatigue Behavior of Titanium and Commercial Titanium Alloys.** C. B. DITTMAR, G. W. BAUER AND D. EVERS. Mallory-Sharon Titanium Corp. U. S. Wright Air Development Center, Tech. Rept. 56-304, January, 1957, 83 pp.

Investigation of effect of microstructure on fatigue behavior of alloys titanium-5 aluminum-2.5 tin, titanium-6 aluminum-4 vanadium and titanium-3 manganese Complex. Microstructure had little effect on endurance limit of alloys unless structure was extremely coarsened or embrittled. Effect of interstitial contents representative of basis for commercial titanium specification, .07 nitrogen, .20 oxygen and .20 carbon taken singly or grouped together was investigated for unalloyed titanium and alloys titanium-5 aluminum-2.5 tin, titanium-6 aluminum-4 vanadium and titanium-3 manganese Complex. Titanium and 3 titanium alloys showed increased or unchanged fatigue life at all interstitial contents specified above. Graphs, tables, photomicrographs.—INCO.

13771

### 6.3.15, 7.6.1

**Titanium Moves Into Process Equipment.** G. T. BEDFORD, W. J. WEEKS. AND

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A. G. Caterson. Rem-Cru Titanium. *Chem. Eng.*, **63**, No. 12, 238, 240, 242, 244, 246, 248 (1956) Dec.

In next 5-10 years demand from chemical processing industries will surpass aircraft for titanium. Advantages of titanium include distinctly better corrosion resistance than common engineering metals in sea water, moist chlorine, metallic chlorides, bleaching solutions and acids; resistance to stress corrosion; and lighter weight without sacrificing strength. Summarized in text and in tables are type of titanium equipment used in various processes, comparison of costs of titanium and Type 316, important physical and mechanical properties of titanium, widely used titanium alloys and their characteristics, and latest corrosion data on titanium listing about 65 organic and inorganic chemicals and corrosive agents. Photograph shows titanium-lined barrel of chlorine dioxide mixer at Riegel Paper Co.—INCO.    13509

**6.3.15**

**Development of Titanium-Base Alloys for Elevated Temperature Application.** W. F. Carew, F. A. Crossley and D. J. McPherson. Armour Research Foundation. Wright Air Development Center, May, 1956, 101 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington, D. C. (Order PB 121467).

The effects on the mechanical properties of a promising alpha-beta type alloy, titanium-6 aluminum-3 molybdenum, of complexing the alpha and beta phases were determined. The alpha complexers tin and zirconium improved the creep resistance and rupture strength of the alloy. The beta complexers chromium, manganese and vanadium used as partial substitutes for molybdenum as the base material, reduced the parameters below the levels of the base composition. Data compiled so far on the creep rupture properties indicate that titanium-aluminum-silver alloys are inferior to binary titanium-aluminum alloys.    13563

**6.3.15, 3.7.3, 3.5.8, 2.3.7**

**Investigation of Stress Relief Procedures for Titanium and Titanium Alloys.** F. J. Gillig. Cornell Aeronautical Laboratory, Inc. U. S. Wright Air Development Center, August, 1956, 82 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 121570).

This investigation was concerned with the causes and effects of residual stresses in titanium aircraft parts and with development of thermal treatments to relieve the stresses. Fundamental principles for the build-up of residual stresses are reviewed. The difference between macro and micro stresses and the relationship between these stresses and the properties of the material are discussed. A method is outlined for setting up simulated residual stresses in a simple beam specimen and measuring their decay with time and temperature. Using the method, relaxation tests were made on four titanium compositions—A-55, C-110M, 6 Al-4V and A-110AT. Recommended stress relief treatments for the four alloys are evolved from test results.    13597

**6.3.15, 3.7.3, 1.6**

**Welding of Titanium and Titanium Alloys.** G. E. Faulkner and others. Titanium Metallurgy Lab., Battelle Memorial Institute, February, 1956, 82 pp. Available from Office of Technical

Services, U. S. Department of Commerce, Washington 25, D. C. (Order PB 121609).    13598

**6.3.15, 3.7.3**

**A Discussion of the Design of Riveted and Bolted Joints in Titanium Sheet.** S. A. Gordon. Titanium Metallurgy Lab., Battelle Memorial Institute, Feb., 1956, 31 pp. Available from Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C. (Order PB 121611).    13600

**6.3.15**

**Properties of Active Eutectoid Titanium Alloys.** R. F. Bunshah and H. Margolin. New York University Research Division. Wright Air Development Center Pubn., June, 1956, 70 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 121481).

Active eutectoid systems, such as titanium-nickel or titanium-copper, hold interest because of the temperature stability of an alpha-plus-compound alloy and because control of particle size should permit control of strength properties over a range of temperatures. In this recent research, microstructure and mechanical properties of titanium-5 copper-3 aluminum, titanium-8 copper-3 aluminum, titanium-5 copper-3 aluminum-2 tin and titanium-8 copper-3 aluminum-2 tin alloys were studied. Room and elevated-temperature properties were found comparable to those of some annealed commercial alloys, with titanium-5 copper-3 aluminum-2 tin showing the best properties. A stable alpha-plus-compound structure showed the best combination of strength and ductility. Microstructure and mechanical properties of binary titanium-nickel alloys were found to be similar to those of binary titanium-copper alloys. Preliminary data on a binary titanium-2 copper alloy showed a considerable increase in strength without loss of ductility after suitable prestrain and anneal treatment.    13537

**6.3.15, 3.7.3**

**Brazing and Soldering of Titanium.** W. J. Lewis, G. E. Faulkner and P. J. Rieppel. Titanium Metallurgy Lab., Battelle Memorial Institute, June, 1956, 28 pp. Available from Office of Technical Services, U. S. Department of Commerce, Washington 25, D. C. (Order PB 121616).    13648

**6.3.15, 1.6**

**The Corrosion of Titanium.** D. W. Stough, F. W. Fink and R. S. Peoples. Battelle Memorial Institute, October 29, 1956, 184 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington, D. C. (Order PB 121601).

The corrosion properties of titanium and some titanium alloys are reported. The data were obtained from the results of laboratory investigations and from reports of the behavior of titanium in service. Included are corrosion rates in various environments, a description of industrial and military corrosion experiences with titanium and the results of fundamental studies of the corrosion and passivating processes on titanium. (auth)—NSA.    13724

**6.3.15, 1.6**

**The Effects of Interstitial Contaminants on the Notch-Tensile Properties of Titanium and Titanium Alloys. Part 2. Alloy Titanium.** E. P. Klier and N. J. Feola. Syracuse University. U. S. Wright Air Development Center, August, 1956, 202 pp. Available from Office of Technical Services, U. S. Dept. of Commerce, Washington 25, D. C. (Order PB 121575).

Tensile and notch-tensile properties of six titanium alloys contaminated with carbon, oxygen, and nitrogen are given for temperatures ranging from 75 to minus 320 F. Notch sensitivity of the various alloys was shown to depend on tensile strength, with the critical strength level falling in the 140,000 to 160,000 psi range. Alloy content and metallurgical structures were found to profoundly

affect the notch sensitivity of the titanium alloys. The effects of testing temperature, contamination level and strain rate on promoting notch sensitivity in the respective alloys are also discussed.
13619

### 6.3.16, 6.6.6
**"β-Tungsten" as a Product of Oxide Reduction.** G. MANNELLA AND J. O. HOUGEN. *J. Phys. Chem.*, **60**, 1148-1149 (1956).

β-tungsten identified on surface of tungsten oxide pellets which were partially reduced at low temperatures. From results β-tungsten appears to be a low-temperature form of tungsten metal.—BNF.
13626

### 6.3.17, 2.3.4, 3.4.6
**A Study of the Reaction Rate Between Tuballoy Metal and Purified Hydrogen.** R. P. STRAETZ and J. E. DRALEY. Chicago Univ. U. S. Atomic Energy Comm. Pubn., CT-3044, June 20, 1945 (Declassified January 5, 1956), 22 pp. Available from Office of Technical Services, Washington, D. C.

Early investigations showed that hydrogen played an important role in the corrosion of jacketed tuballoy (uranium) slugs in aqueous medium. In an effort to afford an understanding of these phenomena, an investigation was undertaken to determine the rate of reaction of purified hydrogen at atmospheric pressure with clean tuballoy metal and tuballoy alloys at temperatures ranging from room temperature to 300 C. The reaction of tuballoy hydride with hydrogen saturated water and the development of methods of handling hydride were also studied. Results are tabulated and the test equipment is described and illustrated photographically. (auth)—NSA.
13922

### 6.3.17, 3.2.3
**Oxidation of 50 Weight Percent** *Uranium-Zirconium Alloy.* SIDNEY BARNARTT, ROBERT G. CHARLES and EARL A. GULBRANSEN. Westinghouse Electric Corp., Pittsburgh. *J. Electrochem. Soc.*, **104**, No. 4, 218-221 (1957) April.

The reaction of 50% uranium-zirconium with oxygen at 1 atm. pressure was studied over the range 200 to 500 C. Two forms of the alloy, the stable ε-phase and the quenched ϑ phase, were reacted to an oxide-scale thickness of 0.1 mm at the higher temperatures. In general, the weight gain increased linearly with time, although in many cases the oxidation curve showed a bend and could be represented by two straight lines. At 400 C and above, the stable ε-phase reacted considerably faster than the ϑ phase. The thick oxide scales were porous and showed uranium enrichment. During the formation of thin oxide films at 200 and 250 C the reaction followed the parabolic rate law approximately. The alloy oxidizes somewhat more rapidly than pure zirconium, but very much more slowly than uranium. (auth).—NSA.
14071

### 6.3.18
**Electrical Thermoelectric Hardness, and Corrosion Properties of Vanadium-Base Alloys.** H. J. CLEARY. Nuclear Metals Inc. U. S. Atomic Energy Comm. Pubn., NMI-1161, Sept. 5, 1956, 34 pp. Available from Office of Technical Services, Washington, D. C.

Attempts have been made to find properties of vanadium metal that make it suitable for industrial use and thereby increase the market for vanadium which is now a by-product of uranium min-

ing. Additions of 1 at.% palladium and other elements give vanadium some unique properties in the super-conducting range that may lead to use of vanadium in the cryotron, a new type electronic amplifier. A vanadium alloy containing 25 at .% aluminum possesses high electrical resistivity (243 microhm-cm) at room temperature; however, this alloy has little ductility. Studies of the thermoelectric power and corrosion resistance of a number of vanadium-rich alloys containing one atomic percent of a variety of elements revealed no striking or useful properties. (auth).—NSA.
13951

### 6.3.19, 5.3.1
**Zinc: Properties and Uses in Modern Industry.** Canadian Zinc Research and Development Committee. *Can. Mining Met. Bull.*, No. 535, 742-754 (1956) Nov.; *Trans. Can. Inst. Mining Met.*, **59**, 410-422 (1956).

A series of short papers and discussions presented at a forum on various aspects of the zinc industry: "Die Casting, G. O. Fry; Zinc Rolling in Canada, V. A. Lee; Continuous Galvanizing of Steel Bands at Stelco, C. H. Steele; (CSA, ASTM and BSI) Zinc Grades and Specifications, J. D. Carr; Zinc Alloys and Corrosion, R. C. Bell; Research and Development, J. O. Edwards; Zinc: General Trends and Economics, O. C. Wilson.—BNF.
13561

### 6.3.20, 4.6.2, 3.2.3
**Effect of Pre-Oxidation in Oxygen on the Steam Corrosion Behavior or Zircaloy-2.** D. E. THOMAS and S. KASS. *J. Electrochem. Soc.*, **104**, No. 5, 261-263 (1957) May.

The effect of pre-oxidation in dry oxygen gas on the corrosion behavior of Zircaloy-2 and unalloyed zirconium in steam was investigated. In the case of Zircaloy-2, pre-oxidation has no effect on corrosion behavior, the kinetics being the same whether all or part of the total exposure is in oxygen. A transition in kinetics from quasi-cubic to linear occurs in the corrosion of Zircaloy-2 in either medium, indicating that the transition is not associated with corrosion product hydrogen. On the other hand, unalloyed zirconium shows neither transition nor breakaway (spalling) when exposed to oxygen and exhibits breakaway on exposure to steam whether pre-oxidized or not, suggesting that breakaway is associated with corrosion product hydrogen. The phenomena of breakaway and transition are shown to be distinctly different.
13861

### 6.3.20, 4.9.4
**The Anodic Oxidation of Some Dilute Binary Zirconium Alloys.** GEORGE B. ADAMS, JR., CURTIS E. BORCHERS and PIERRE VAN RYSSELBERGHE. Univ. of Oregon. U. S. Atomic Energy Comm. Pubn., AECU-3388, January 1, 1957, 29 pp. Available from Office of Technical Services, Washington, D. C.

The low-potention anodic oxidation of Kroll process zirconium at very small constant ionic currents in aqueous media was described. The apparent electrolytic parameters $\sigma A$., $\sigma B$., the apparent formation field, $F/\sigma$, and estimates of local corrosion currents and oxide film thicknesses were all obtained from potential-time measurements on the very thin anodic films formed in the potential range below oxygen evolution. The present research is an attempt to correlate changes in these measured electrolytic parameters for the anodic oxidation process with changes in alloying con-

stituents for a series of dilute binary zirconium alloys. (auth) —NSA   1407⁵

### 6.3.21
**Crystal Bar Hafnium Powder, Its Production, Mechanical and Corrosion Properties.** C. T. WALDO and W. KERMIT ANDERSON. Knolls Atomic Power Lab. U. S. Atomic Energy Comm. Pubn., KAPL-CTW-2, January 10, 1957, 11 pp Available from Office of Technical Services, Washington, D. C.

Hafnium powder can be produced quite easily by the hydride process in much the same way as zirconium. Specimens fabricated from hafnium powder have poor ductility and a tensile strength of approximately 75,000 psi. The corrosion performance of fabricated powder metallurgy shapes in 680 F water is considered good on the basis of a 4000 hr. exposure. (auth) —NSA   14125

### 6.3.21, 3.8.4, 5.3.4
**The Rate of Reaction of Nitrogen with Hafnium Metal (Technical Report No. 19 on Chemical Thermodynamics of Materials at High Temperatures).** RUSSELL K. EDWARDS and GLENN T. MALLOYI Illinois Institute of Technology, Project 051-070, Contract NONR-1406, December, 1956, 12 pp.

The reaction rate of nitrogen with hafnium metal was studied in the temperature range 876 to 1034 and over the pressure range 38 to 402 mm. The rate of behavior follows the simple parabolic rate law without deviation for the periods of time studied (up to 132 minutes). The activation energy was found to be 57 kcal per mole of nitrogen. A comparison of these results with other results in the literature shows that rates decrease and activation energies increase in the order, titanium, zirconium, hafnium, for the nitridization process with this group of metals. (auth) —NSA
13990

### 6.3.19
**Corrosion Resistance of Zinc Alloys Containing Manganese and Copper.** S. FUJINO. *Repts. Govt. Ind. Res. Inst., Nagoya*, **5**, No. 7, 326-329 (1956) July.

The epsilon phase of zinc-manganese-copper system is stable at high temperatures and is similar to the epsilon phase (hexagonal close packed) of copper-zinc system. This report gives the results of experiments on the corrosion resistance of quenched zinc-copper alloy systems, where the range of added elements is 6-25% for manganese and 0-19% for copper.

Procedure: Volume of hydrogen released from the sample dipped in 1.2 N hydrochloric acid; weight loss of the sample dipped in 3.5% N sodium chloride potassium chloride and 0.1 N hydrochloric acid solutions were measured. Results are as follows:

(1) Alloys containing about 14% copper have good corrosion resistance equal to that of 99.99% zinc.

(2) Alloys containing above 15% copper have better corrosion resistance than 99.99% zinc.

(3) Alloys which showed superior corrosion resistance produced passive films on their surfaces in the solutions. —JSPS.
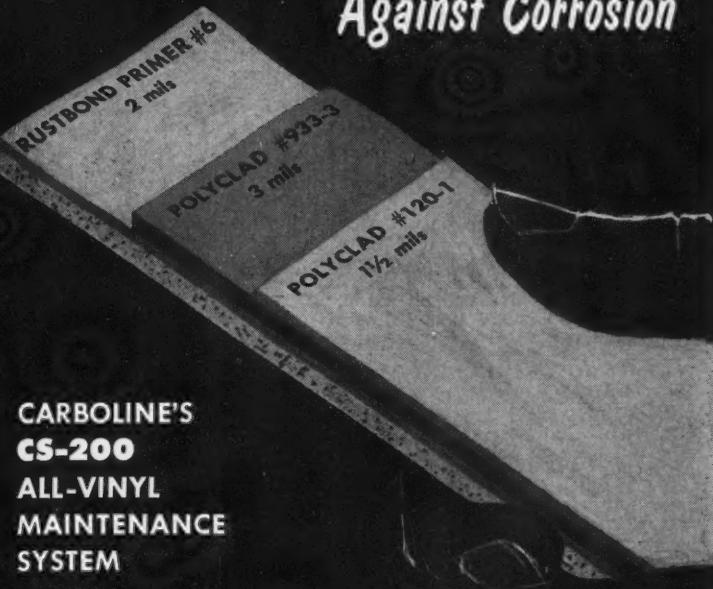13981

### 6.3.20, 3.2.2
**Low-Pressure Solubility and Diffusion of Hydrogen in Zirconium.** M. W. MALLETT and W. M. ALBRECHT. Battelle Memorial Institute. *J. Electrochem. Soc.*, **104**, No. 3, 152-146 (1957) Mar.

Low-pressure solubilities were deter-

mined for hydrogen in α- and β- zirconium and in two zirconium-oxygen alloys at 700 to 1000 C and pressure of 0.1 to 4μ Hg. The data followed Sieverts' law for each phase and hydrogen solubility decreased with increasing temperature at a given pressure. Also, there was a slight increase in hydrogen solubility in α-zirconium with increasing oxygen content. Diffusion coefficents for hydrogen in α zirconium were obtained in the range 300 to 600 C by analysis of prepared concentration gradients. In the range 600 to 800 C, degassing coefficients were determined from rate of hydrogen evolution from zirconium cylinders. Degassing coefficients were much lower than was expected from diffusion theory and it was concluded that the degassing was not a pure diffusion phenomenon. Terminal solubilities obtained from the gradient analysis were in good agreement with those found by previous investigators. (auth)—NSA. 14141

### 6.3.20, 3.5.9
**Oxidation of Zirconium Between 400 C and 800 C.** E. A. GULBRANSEN and K. F. ANDREW. Paper before Am. Inst. Mining Met. Engrs., New Orleans, Feb., 1957. *J. Metals* (Trans. AIME), **9**, No. 4, 394-400 (1957) April.

Work was undertaken to study reaction at 400-800 C to ascertain if change occurs in reaction mechanism between 400 and 600 C to test application of cubic and parabolic rate laws to data for long-time oxidations and for specimens of varying surface preparations and to test reaction mechanism by use of theoretical rate expressions. Results on abraded specimens are best fitted to cubic rate law, while chemically polished specimens conform to parabolic rate law. Oxide film adheres to surface up to 800 C where spontaneous ignition occurred. Classified theory of oxidation and diffusion is applied to data assuming two mechanisms of reaction; fit is obtained with mechanism based on diffusion of zirconium ions in cation vacancies. Tables, graphs. —INCO. 14061

### 6.3.20, 3.5.9
**An Investigation of Scaling of Zirconium at Elevated Temperatures (Quarterly Status Rept. No. 15 for December 2, 1946 to March 2, 1957).** H. B. PROBST, E. B. EVANS and W. M. BALDWIN, JR. Case Institute of Technology. U. S. Atomic Energy Comm. Pubn., AECU-3424, March 6, 1957, 7 pp. Available from Office of Technical Services, Washington, D. C.—NSA. 14048

## 6.4 Non-Ferrous Metals and Alloys—Light

### 6.4.2
**On the Newly Invented Anticorrosive High Strength Aluminum Alloy "SAX."** M. KOSAKI, R. KAWACHI AND T. AMITANI. *Sumitomo Metals*, **9**, No. 1, 1-4 (1957) January.

Addition of copper to an aluminum alloy hardened by precipitation of $Mg_2Si$ has the effect of improving its mechanical properties, but it lowers corrosion resistance of the alloy. Addition of 0.25 copper was heretofore considered maximum. New aluminum alloy (Jap. Pat. No. 227,041, Nov. 11, 1956) contains larger amount of copper, resulting in improved mechanical properties without lowering corrosion resistance. Chemical analysis of SAX alloy is the

following: 0.66 copper-1.17 magnesium-0.008 manganese-0.35 iron-0.60 silicon-0.01 zinc-0.39 chromium-0.16 cadmium-0.048 titanium-balance aluminum. Tables summarize mechanical properties after various heat treatments and after corrosion test in concentrated sodium chloride-0.3 hydrogen peroxide; comparative data are given for 61S alloy. Graphs.—INCO. 14205

### 6.4.2, 3.2.2
**Intercrystalline Corrosion, Due to Hydrochloric Acid, of Aluminum Purified by Zone Melting.** (In French.) FREDERIC MONTORIOL. *Compt. Rend.*, **244**, No. 16, 2163-2166 (1957) April 15.

Samples of super purity Al prepared by zone melting were subjected to various heat treatments and subsequently exposed to the corrosive attack of a 22% solution of hydrochloride acid. Samples annealed at 600 C and slowly cooled exhibited an extremely slow corrosion process and retained the brightness of the electrolytic polish for about 80 days of immersion. The grain boundaries of quenched samples, on the other hand, were rapidly attacked. Anodic corrosion produced geometric figures of exceptional regularity. Minute additions of copper iron (0.5 parts to the million) to the corrosive medium had an accelerating effect on the process. Summing up it is said that super purity aluminum prepared by zone melting exhibits an intercrystalline corrosion behavior different from that of high purity aluminum, even if the latter metal's purity is superior to 99.994%.—ALL. 14139

### 6.4.2, 3.4.9, 5.4.2
**The Formation of Films on Aluminum Immersed in Water.** R. K. HART. *Trans. Faraday Society*, **53**, Pt. 7, 1020-1027 (1957) July.

High-purity aluminum, when subjected to total immersion at 20 to 80 C in pure water carries surface films which are either "amorphous" or crystalline hydrates. Below a critical temperature, between 60 and 70 C, film growth proceeds in three stages. (1) "amorphous"; (2) boehmite, γ — AlO(OH); orthorhombic, a = 3.78 Å, b = 11.8 Å, c = 2185 Å; and (3) bayerite, β — $Al_2O_3 \cdot 3H_2O$; monoclinic, a = 4.72 Å, b = 8.68 Å, c = 5.06 Å, a = 90° 11', the final film thus consisting of three layers. Above the critical temperature only boehmite films are formed on the top of the initially present amorphous film. Oriented overgrowth is favored by both boehmite and bayerite: (001) parallel to the surface for boehmite, and (010) parallel to the surface for bayerite. Immersed aluminum is almost immune to pitting; it does, however, suffer severe intergranular attack, especially above 60 C.—ALL. 14287

### 6.4.2, 3.7.2, 2.3.1
**Chromium and Manganese Contents in Light Alloys Containing Aluminum and 3% or 5% Magnesium.** (In French.) A. GUILHAUDIS AND R. DEVELAY. *Rev. Met.*, **54**, No. 4, 288-298 (1957) April.

Results of investigations concerning the effect of chromium and manganese additions on the tensile strength, deep drawing properties, weldability and resistance to corrosion of aluminum alloys containing 3% or 5% magnesium, are reported. The method of preparation of the alloys and samples, also the test equipment and testing procedure are described. It appears that, generally speaking, chromium and manganese additions have a favorable influence on

mechanical and welding properties and also on the resistance to corrosion of alloys of the aluminum-3% magnesium type. Best results were obtained with 0.15 to 0.25% chromium and 0.30 to 0.45% manganese. The aluminum-5% magnesium alloys tested exhibited inferior welding characteristics and an increase in manganese and chromium contents does not seem necessarily to induce an improvement in corrosion resistance. On the whole, the most beneficial additions are 0.10 to 0.15% chromium and 0.15 to 0.25% manganese. It is believed that further improvements could be obtained by a suitable amount of silicon, as well as the chromium and manganese.—ALL. 14279

### 6.4.2, 3.7.3
**The Heat-Treatment of Light Alloys.** T. R. G. WILLIAMS. *Rev. Met.*, **53**, No. 10, 791-795 (1956).

Williams studied the problems that arise in the heat-treatment of extruded and rolled aluminum and aluminum alloys. He describes some of the factors governing the choice of equipment and method of treatment adopted for the solution-treatment, annealing, ageing and stress-relieving under the headings of metallurgical and non-metallurgical factors. Among the former, rates of heating and cooling and soaking times and temperature are considered in relation to the properties of the material, i.e. recrystallization temperature, melting temperature, mechanical strength and susceptibility to corrosion. The latter include staining, mechanical damage and distortion on quenching. He describes and compares present furnace designs and suggests some possible future developments. 16 references.—MA. 14037

### 6.4.2, 3.7.3
**Removal of Oxide from Aluminum by Brazing Fluxes.** M. F. JORDAN and D. R. MILNER. *J. Inst. Metals*, **85**, Pt. 2, 33-40 (1956) October.

Study of fringe systems set up by interference of monochromatic light reflected from metal with that reflected from any partially detached oxide. Rate of potential decay is related to flux efficiency as shown by measurements of potential of oxide coated aluminum made during course of fluxing action. An electrochemical theory is advanced. —BL. 14040

### 6.4.2, 3.7.3
**Investigations on Macrostructure and Strength Properties of Aluminum-Copper-Magnesium and Aluminum-Zinc-Copper-Magnesium Alloy Press Forgings.** (In German.) WILHELM ROSENKRANZ. *Z. Metallkunde*, **48**, No. 2, 41-53 (1957) Feb.

The effect of production variables, such as heat treatment and the rate and temperature of deformation on macrostructure, static and dynamic strength characteristics and corrosion properties of press forgings, was investigated. Sections of CCP cast metal were press-forged to wedge-shape test-pieces by using hydraulic, toggle and spindle presses. The temperature of the dies was 150 C for the latter types of presses, which for the hydraulic press-forging operation dies at 380, 430 and 470 C temperature were used. Subsequent to solution heat treatment the differential evolution of recrystallization was

studied. To investigate the tensile strength and fatigue resistance of such forgings, test bars were prepared both from the central and from the marginal zone of the wedges. The results are said to have corroborated the correctness of the view that those materials which, prior to solution heat treatment, lend themselves readily to recrystalization or recovery, are likely to exhibit better fatigue properties in the aged condition. Since, in aluminum-zinc-copper-magnesium alloys the grain boundaries are more towards the less noble end of the electrochemical series than is the solid solution itself, such alloys, if recrystallized, show a tendency to stress corrosion, while for aluminum-copper-magnesium alloys the opposite holds. The quality of the forged product and the type of press which appears to be most suitable for attaining the quality, has to be determined by taking all these properties into consideration.—ALL.
13870

### 6.4.2, 3.8.2

**Electrochemical Behavior of Aluminum. Potential-pH Equilibrium Diagram of the System Aluminum-Water, at 25C.** (In French) E. DELTOMBE AND M. POURBAIX. Centre Belge d'Etude de la Corrosion, Rapport Technique No. 42, December, 1956, 20 pp.

On the basis of free enthalpies of standard formation of various constituents of the aluminum-water system, an equilibrium diagram according to the pH and the electrode voltage at 25 C was made. Corrosion, passivation and stability of aluminum were studied.—BTR.
14000

### 6.4.2, 4.6.1, 3.6.8

**Mechanisms of Aqueous Corrosion of Aluminum at 100 C.** K. M. CARLSEN. Paper before Electrochem. Soc., Cleveland, September 30-October 4, 1956. *J. Electrochem. Soc.*, 104, No. 3, 147-153 (1957) March.

Superpurity aluminum, 1 nickel-aluminum, 2 copper-aluminum, 1 iron-aluminum and 1 silicon-aluminum alloys were tested in aqueous solutions at 100 C. Samples were polarized cathodically and anodically to study effect of cathodic and anodic reactions on corrosion behavior. Eutectic $NiAl_3$ is preferentially attacked both on cold worked and annealed specimens on exposure to 100 C water, while aluminum matrix is only slightly attacked. At 230 C, eutectic regions are again attacked and matrix corrodes in more general manner. When 1 nickel-aluminum alloys are made cathodes at 0.1 ma/cm² they are severely attacked in eutectic regions and anodic samples develop pitting. Results are interpreted as showing that alkalinity produced at cathodes facilitates film breakdown in these places. Polycrystalline superpurity aluminum was attacked in grain boundaries. Reported success of aluminum-iron, aluminum-nickel and aluminum-copper alloys indicates that alloying elements protect metal by providing sites for cathodic reactions. Effect of silicon is not understood. Influence of bulk pH and inhibitors is discussed. Numerous photomicrographs. —INCO.
13901

### 6.4.2, 4.6.7, 3.5.9

**Thermogalvanic Potentials and Currents at Aluminum Surfaces in Industrial Water.** EDGAR C. PITZER. *J. Electrochem. Soc.*, 104, No. 2, 70-74 (1957) Feb.

Potentials and galvanic currents at 2S

aluminum surfaces in Columbia River water were studied between room temperature and 100 C. The aluminum potential changed by approximately 0.6 v over this interval, becoming more anodic with increase in temperature. Similar but somewhat smaller changes in potential were noted in buffer solutions.

By coupling identical aluminum samples, one at 100 degrees and the other at room temperature, a maximum current density of 40 μamp/cm² was maintained.
13830

### 6.4.2, 6.2.4

**Fatigue Tests on Notched and Unnotched Sheet Specimens of 2024-T3 and 7075-T6 Aluminum Alloys and of SAE 4130 Steel with Special Consideration of the Life Range from 2 to 10,000 Cycles.** W. ILLG. U. S. National Advisory Commission for Aeronautics, Tech Note No. 3866, December, 1956, 40 pp.
14038

### 6.4.2, 6.6.11, 4.6.11, 5.4.8

**The Performance of Alcan 65S-T6 Aluminum Alloy Embedded in Certain Woods Under Marine Conditions.** T. E. WRIGHT, H. P. GODARD AND I. H. JENKS. *Corrosion*, 13, No. 7, 481t-487t (1957) July.

Laboratory and marine exposure tests were carried out to assess the performance of Alcan 65S-T6 (6061-T6) aluminum alloy embedded in certain woods under marine exposure conditions. The tests also involved the assessment of several protective paint systems designed to protect the wood in the simulated hull sections used in the tests.

The relative corrosivity to aluminum of the woods tested under ship hull conditions is: rock elm (least), mahogany and British Columbia fir (most). Only very slight corrosion occurs when the aluminum is coated with zinc chromate priming paint even in the most corrosive woods after extended immersion periods in sea water. Alcan 65S-T6 (6061-T6) has a corrosion resistance greatly superior to that of Alcan 24S-T3 & 4 (2024-T3 & 4) under the same marine exposure conditions. Anodizing increases the corrosion resistance of both alloys, particularly if this treatment is followed by a coat of zinc chromate primer. The use of wooden dowels to protect aluminum embedded in these woods is also beneficial. Among the variations in paint systems which were tested, the most complete paint system, comprised of sealer + barrier layer + copper antifouling paint provided maximum protection from corrosion. Where pitting occurred on 65S-T6 (6061-T6) embedded in sea water wetted wood, it has been shown that the rate of penetration falls off sharply with time.
13935

### 6.4.2, 8.8.1

**Aluminium in the Construction of Chemical Processing Apparatus.** E. MOOR. *Aluminium Suisse*, 7, No. 2, 43-56 (1957) March.

In this first installment of a series of articles on the use of aluminum in the construction of chemical processing apparatus some introductory remarks are made concerning the importance and possible applications of aluminum in this field. Then, the properties of aluminum are briefly discussed and compared with those of other metals. Corrosion behavior and strength characteristics of various wrought and cast aluminum alloys are tabulated and hence conclusions are drawn concerning design principles. Formulæ and constants are

given to be used in the calculation of welded cylinders of different designs.—ALL.
1412

### 6.4.2, 8.9.2

**Resistance to Corrosion of Aluminum Alloys for Automotive Applications.** E. T. ENGLEHART, W. C. COCHRAN AND E. P. WHITE. *Corrosion*, 13, No. 9, 555t-560t (1957) Sept.

Aluminum alloys have been employed in automobiles for some time in applications such as pistons. In recent years, however, increased use of aluminum alloys for many other automotive applications has been anticipated. This paper presents the available information on the resistance to corrosion of aluminum alloys for these many new uses. Particular emphasis has been placed on performance of aluminum alloys for automotive trim, but other applications are also covered. Included is a discussion of choice of alloy and the performance of the large variety of finishes available. Results of atmospheric corrosion tests together with those of limited field experience are provided to indicate the good resistance to corrosion of aluminum alloys in these applications. Factors affecting the performance of these alloys in service are also covered. 14193

### 6.4.3, 4.6.1

**Corrosion of Beryllium in 525 F and 600 F Distilled Water.** R. S. PEOPLES AND H. BULKOWSKI. Battelle Memorial Institute. U. S. Atomic Energy Comm. Pubn., BMI-HAP-101, Sept. 12, 1949 (changed from Office Use Only January 11, 1957), 17 pp. Available from Office of Technical Services, Washington, D. C.

Corrosion tests were conducted on sintered grade and vacuum-cast extruded beryllium specimens. Results indicate that the sintered grads is more resistant to disintegration and localized attack than extruded material.—NSA.
13834

### 6.4.2

**Mechanical Tests on Specimens from Large Aluminium-Alloy Forgings.** J. A. MILLER AND A. L. ALBERT. U. S. National Advisory Committee for Aeronautics, Tech. Note No. 3729, August, 1956, 25 pp.

Results of tensile and bend tests on specimens from solution heat treated and artificially aged hand forgings of aluminum alloys (aluminum-5.6 zinc-4.4 copper-0.8 silicon-0.8 manganese-0.3 chromium and aluminum-5.6 zinc-2.5 magnesium-1.6 copper-0.3 chromium). Stress and strain at failure varies with location and direction of specimen in forging, effects of biaxial tensile stress conditions, etc.—BNF.
13268

### 6.4.2

**Finishing Systems for Aluminum.** R. V. VANDEN BERG. *Elec. Mfg.*, 58, 150-155, 292, 295 (1956) Oct.

Surface finishes produced by mechanical, chemical and electrochemical methods, besides painting and porcelain enameling are discussed.—BTR. 13412

### 6.4.2

**Finishing Aluminum.** R. C. SPOONER AND J. LOUCKS. *Modern Metals*, 12, No. 6, 62-70 (1956) July.

Techniques include mechanical, chemical, electrochemical and coating. Choice of technique depends on appearance, resistance to weathering or corrosion, hardness or wear resistance and the presence or absence of color.

Methods and applications are discussed.—RAD.
12618

### 6.4.2, 3.5

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### 6.4.2, 3.5.8
**On the Problem of Intercrystalline Corrosion of Wrought Aluminium-Magnesium Alloys.** E. Hugony and M. Monticelli-Papania. *Alluminio*, **25**, No. 9, 373-384 (1956) September.

Results of research work carried out on the tendency of aluminum-magnesium alloys to stress corrosion is reported. The ultimate object of the tests performed was to define the alloying composition which exhibits highest resistance to corrosion when subjected to the combined action of a corrosive medium and mechanical stress, as it is in the case of most naval applications. Laminated specimens of twelve different aluminum-magnesium alloys with small manganese, iron, silicon and chromium contents were subjected to loop-tests in a 3% sodium chloride and 1% hydrochloric acid solution and the effects of both temperature and conditions of heat treatment were observed. Taking into consideration some secondary factors, such as work hardening and service conditions above room temperature (50 C), and also the further necessity of preserving, as far as it is possible, the mechanical characteristics of the alloy, the proportion of magnesium recommended is 4.4%. A discussion on the subject is reproduced in detail. An extensive bibliography is presented.—ALL.
13177

### 6.4.3, 4.6.1
**Corrosion of Sintered and Extruded Beryllium at 550 F in Distilled Water (1030 psi).** R. S. Peoples, H. Bulkowski and F. W. Fink. Battelle Memorial Institute. U. S. Atomic Energy Comm. Pubn., BMI-HAP-102, Jan. 18, 1950 (Changed from Official Use Only Jan. 11, 1957), 7 pp. Available from Office of Technical Services, Washington, D. C.

Evidence of corrosion damage was found in all samples of sintered and vacuum cast-and-extruded beryllium. It was concluded from results of tests that 550 F is beyond the safe limit for the material tested.—NSA.
13832

### 6.4.4, 3.5.9, 3.4.9
**Oxidation of Magnesium by Air Between 350 and 500 Degrees.** (In French.) M.-L. Boussion, L. Grall and R. Caillat. *Rev. Met.*, **54**, No. 3, 185-188 (1957) Mar.

To test the suitability of commercial purity magnesium as a cladding material in nuclear reactors corrosion tests were carried out in humid air saturated at 25 C, at temperatures ranging from 350 to 500 C. The increase in weight of the etched and chemically brightened samples was determined by the discontinuous and also by the continuous thermogravimetric methods. The maximum operating temperature for magnesium in a moist atmosphere and in the absence of radiation is set at 350 C. The kinetic problems of oxidation in water vapor are investigated. It is said that basic processes are still not well understood. Three different reactions may occur: oxidation, nitridation and reduction of water vapor.—ALL.
14055

### 6.4.4, 3.7.2
**The influence of Impurities on Some Properties of High Purity Magnesium. Part II. Some Mechanical Properties and Corrosion Resistance.** (In Japanese.) Riei Ichikawa. *Light Metals* (Japan), No. 23, 50-53 (1957) March.

Influence of impurities in magnesium on some mechanical properties and corrosion resistance was studied for super purity magnesium prepared by vacuum evaporation process, high purity magnesium containing several alloying impurities, and commercial purity magnesium. The results obtained are as follows: (1) Fair deformability was obtained with super purity magnesium. (2) The change in mechanical properties depending upon the change of kinds and quantity of impurities in magnesium was not remarkable, but copper and silicon slightly reduce deformability of magnesium. (3) Superior corrosion resistance was obtained in the case of super purity magnesium. (4) The corrosion resistance of high purity magnesium fell off in order of aluminum, silicon, copper and iron contained in magnesium. (5) In case of commercial purity magnesium, the corrosion resistance was inferior, but better than magnesium containing some quantity of iron. —ALL.
14233

### 6.4.4, 3.7.2
**Effect of Zirconium on Several Properties of Magnesium Alloys.** F. A. Borin and E. S. Sollertinskaya. *Metallovedenie i Obrabotka Metallov* (U.S.S.R.), No. 2, 8-13 (1956); *Chem. Absts.*, **51**, No. 1, 191-192 (1957) January 10.

The alloys studied were magnesium-zirconium, containing 0.38 to 0.67 zirconium and 0.008 max. iron, and magnesium-zinc-zirconium, containing 4.16 to 4.86% zinc, 0.06 to 0.67 zirconium, and 0.026 max. iron. The zirconium was added as a mixture of potassium fluozirconates. A temperature of 900 C was needed for its absorption, but, at best, the efficiency of addition was only 25%.

Effects on yield strength, tensile strength, elongation, reduction, ductility, high temperature strength and corrosion resistance are covered. —ALL.
13923

## 6.5 Metals—Multiple or Combined

### 6.5
**High Alloys to Combat Corrosion.** E. D. Weisert. *Corrosion*, **13**, No. 10, 659t-671t (1957) October.

The use of highly alloyed materials to combat corrosion is discussed and extensive data are given. The following molybdenum-bearing alloys are considered at length: nickel-molybdenum alloy, nickel-molybdenum-chromium alloy and nickel-chromium-iron-molybdenum alloy. Attention is given also to cobalt-base alloys and silicon-bearing alloys. Other matters considered in connection with these alloys include mechanical properties, welding characteristics, pre-welding considerations, welding techniques, general fabrication considerations and heat treatment.
14254

### 6.5
**Progress Report in Metallurgy for April 1, 1950 to September 30, 1950.** B. A. Rogers. Ames Lab. U. S. Atomic Energy Comm. Pubn., ISC-128, Nov. 10, 1950 (Declassified Jan. 5, 1956), 41 pp. Available from: Office of Technical Services, Washington, D. C.

Progress is reported in the following studies: the distillation and preparation of calcium; the preparation, casting and fabrication of zirconium; the preparation of consumable electrodes; corrosion of zirconium and zirconium alloys; the preparation of vanadium by fused salt electrolysis; and the preparation and properties of alloys of uranium-zirconium, thorium-zirconium; niobium-zirconium, tin-zirconium, aluminum-zirconium,

germanium-zirconium and thorium-uranium and carbon-thorium systems. Constitution diagrams are presented for the carbon-thorium system and thorium-zirconium, tin-zirconium, and thorium-uranium alloys.—NSA.                13365

### 6.5, 3.5.9
**Actual Metallurgical Problems in High-Temperature Alloys.** W. SIEGFRIED. *Metaux: Corrosion-Industries*, **31**, 418-431 (1956) Oct.

Discussion on properties required of materials used in various components of gas turbines. Review of recent developments in ferritic and austenitic high-temperature materials includes tabulation of compositions and stress-rupture properties of K42B, 19/9 DL, various high- and low-alloy nickel-chromium and nickel-chromium-molybdenum steels, Lapelloy, German steels designated "Witten" and "Thum," A-286, S-816, Inconel X, M-252, Nimonic 80, Nimonic 90, G32, Haynes Alloy Nos. 21, 25 and 31 and TC-661 (50% Inconel infiltrated titanium carbide).—INCO.                13387

## 6.7 Duplex Materials

### 6.7.2, 5.9.1
**Preliminary Investigation of the Effect of Surface Treatment on the Strength of a Titanium Carbide-30 Percent Nickel Base Cermet.** L. ROBINS AND E. M. GRALA. Lewis Flight Propulsion Lab. U. S. National Advisory Comm. for Aeronautics, Tech. Note 3927, February, 1957, 16 pp.

Investigation of effects of grinding, lapping, blast cleaning, acid roughening, oxidizing and refinishing on room-temperature modulus of rupture and impact strength of a nickel-bonded titanium carbide cermet. Most serious losses occurred after oxidation, surface roughening by acid attack and severe grinding with a 60 grit silicon carbide abrasive wheel. Modulus of rupture strength of oxidized specimens was improved after grit blasting or regrinding with a diamond abrasive wheel. Photomicrographs, graphs, tables. —INCO
13827

## 7.    EQUIPMENT

## 7.2 Valves, Pipes and Meters

### 7.2, 8.4.5
**On the Quality Requirements for Steel Valves for Nuclear Power Plants.** J. J. KANTER. Paper before 2nd Nuclear Eng. & Science Conference, Philadelphia, Mar. 11-14, 1957; Am. Soc. Mech. Engrs. Paper No. 57-NESC-33, 1957, 5 pp. *Valve World*, **60**, No. 1, 20-26 (1957).

Discussion of considerations and problems encountered in making available steel primary loop valves suitable for conditions of nuclear power plants. For each type of reactor, primary loop piping presents a different corrosion problem. In case of water cooled reactors, radiation provides a constant source of dissolved oxygen which together with decomposition products, are factors in steel corrosion. In case of liquid sodium heat transfer, there also exists a problem of attack upon steel and nickel-chromium austenitic steels are deemed necessary to resist it. Where liquid bismuth is the medium, there are mass transfer considerations and chromium-molybdenum ferritic steels have given most favorable performances to date. From standpoint of minimizing corrosive attack, austenitic nickel-chromium

Types 347, 304 and 316 are being used. Well made steel castings are acceptable for primary loop applications as are forgings, although apprehension seems to exist over porosity inherent in steel castings. Surface of stainless valve parts for many of the loops is a special requirement. Rough forged or "as cast" surface must be removed by machining, grinding or filing both inside and out and extensive rework and repair of minor defects is a considerable cost item.—INCO.                14087

### 7.2
**Flow Measurement of Corrosive and Similar Fluids.** A. LINFORD. *Fluid Handling*, Nos. 85, 86, 87, 39-42; 78-80; 98-99, 120 (1957) Feb., March, April.

Description of mechanical displacement type, differential pressure type flow meters and purge system of metering. Applications and descriptions of shunt type, electro-magnetic and ultrasonic type flow meters are given. Photos, diagrams.—INCO.                14078

### 7.2, 4.5.1
**An evaluation of Buried Waste Line Design Fracture. Underground Pipeline and Structure Corrosion Study Program (Interim Report No. 2).** R. T. JASKE. Hanford Atomic Products Operation. U. S. Atomic Energy Comm. Pubn., HW-35009, April 1, 1955 (changed from Official Use Only January 23, 1957), 43 pp. Available from Office of Technical Services, Washington, D. C.

Includes a reprint: **Examination of 335 Miles of Asphalt Mastic Coated Pipe.** DONALD E. MILTNER. *Corrosion*, **9**, 210-215 (1953). —NSA.                13864

### 7.2, 6.6.8
**Experience with Oil Field Extruded Plastic Pipe in 1955.** A Report of NACE Technical Unit Committee T-1J on Oil Field Structural Plastics. (W. B. SANFORD, Chairman). *Corrosion*, **13**, No. 7, 461t-465t (1957) July.

The results of a questionnaire submitted to users of oil field extruded plastic pipe are summarized and evaluated. Fifty-six replies were received of which 16 were from independent producers and 40 from some six major producers. Data contained in the replies pertain to such matters as amount of extruded plastic pipe used by type of material, amount of pipe used by type of service, failure frequency, success in repairing leaks, distribution of failures according to amount of pipe used, cause of failure, reasons operators prefer extruded plastic pipe and economic feasibility of increased use of plastic pipe. Replies received from independent operators and major companies are compiled separately in giving the above data.
13896

### 7.2, 6.6.8
**Thermoplastic Materials for Pipe.** P. M. ELLIOTT. *Corrosion*, **13**, No. 10, 647t-653t (1957) October.

The general properties of plastic pipe are outlined and comparisons made with metal pipe. Particular attention is given to polyethylene, acrylonitrile copolymer blends, cellulose acetate butyrate, polyvinyl chloride and polyvinylidene chloride. Heat distortion temperatures and range of recommended temperatures are given for these materials. Data showing rate of testing versus fiber stress at burst, fiber stress versus time to fail, hoop stress versus service life, tensile stress versus time to rupture, fiber stress at burst versus temperature, ten-

sile strength versus temperature and safe hoop stress versus temperature are given for some of these plastics. The joining of plastic pipe is discussed briefly. Other topics considered include long term effects of stresses, temperature effects and new developments in plastic piping.                14258

### 7.2
**Design of an Experimental Ball Valve.** A. SOBOLEV. *J. Inst. Water Engrs.*, **10**, No. 7, 552-557 (1956) Nov.

Main objects in developing design: reduction of cavitation including comparative values of resistance to cavitation in sea water of 60/40 brass, stainless steel, nylon and aluminum bronze (88.7 copper-11.1 aluminum-0.8 manganese): elimination of "sticking"; simplicity and robustness.—BNF.                1366

## 7.3 Pumps, Compressors, Propellers, Impellers

### 7.3.2
**What Are Heater Tubes Worth?** R. B. SMITH and R. R. EDISON. Sinclair Res. Labs. *Petroleum Refiner*, **35**, No. 8, 133-140 (1956) August.

Method for finding most economical tube temperature, wall thickness and corrosion allowance when process conditions set tube size, heat load and outlet temperature. Minimum thickness of tube wall is calculated from code and corrosion allowance is added. Equation shows that for any given minimum tube wall thickness optimum corrosion allowance is a function of corrosion rate, stipulated return and fixed charges. Graphs, tables.—INCO                13088

### 7.3, 3.5.8
**Influence of Asymmetrical Loading Upon the Corrosion Fatigue Resistance of Pumping Rods.** (In Russian.) R. M. RASKIN AND R. A. BAGRAMOV. *Vestnik Mashinostroeniia*, **37**, No. 1, 28-30 (1957) January.

Experiments show that during corrosion fatigue, the over-all amplitude of steel 40 U pumping rods remains constant with an increase of asymmetry. With increasing asymmetry of the cycle, the relative lowering of corrosion-fatigue resistance diminishes. 3 references. —MR.                14172

### 7.3, 7.1, 6.3.11
**Evaluation of Gold and Gold Alloy Bearings in Process Pumps.** J. DUNN. Hanford Atomic Products Operation. U. S. Atomic Energy Comm. Pubn., HW-41727, February 13, 1956, 10 pp. Available from Office of Technical Services, Washington, D. C.

The test results for gold, gold-copper-silver and gold-copper bearings against various journals in deepwell turbine pumps and chempumps are tabulated and discussed.—NSA.                13880

## 7.4 Heat Exchangers

### 7.4.1
**Design Aspects of High-Pressure Feedwater Heaters.** J. M. WEST. Paper before Am. Power Conf., 18th Ann. Mtg., Chicago, March 21-23, 1956. *Proc. Am. Power Conf.*, **18**, 250-254 (1956).

Pressure parts are largely low carbon steel plate and forgings. Tube materials include 90-10, 80-20 and 70-30 copper-nickel and Monel. Desuperheat zone in-

let nozzle usually contains a stainless steel liner to isolate steam from shell and adapter region. A stainless steel burning ring surrounds tube bundle adjacent to joint so that joint may be cut without damage to tubes. Welded tube joints on special types of heat exchangers are clad first with Monel welding rod and final weld is made between tube wall and cladding. Diagrams, graphs. —INCO.                              13717

## 7.5  Containers

### 7.5.5, 5.4.3, 8.8.5
**Tank Linings (for Pickling and Plating Tanks).** K. G. LE FEVRE. *Tech. Proc. Am. Electroplaters' Soc.,* **1956,** 34-40, 286, 287.

Thin linings (synthetic resins, sprayed metals or combination coatings of sprayed metal sealed with organic coating); thick linings (bitumens and plastisols, i.e., dispersons of finely divided vinyl resins and plasticizers); and (most detailed section) sheet linings (rubber, neoprene, polyvinyl chloride, Kel-F, etc.). Properties, economics and other aspects.— BNF.                                  13634

## 8.  INDUSTRIES

## 8.4  Group 4

### 8.4.3
**New equilibrium Data on Sweetening Natural Gas with Ethanolamine Solutions.** H. C. MUHLBAUER AND P. R. MONAGHAN. Paper before Gas Conditioning Conference, Univ. Okla., Norman, March 6, 1957. *Oil Gas J.,* **55,** No. 17, 139-145 (1957) April 29.

Development of data to be used in accurate design of gas-treating plants and in proper operation of these plants. Underestimation of amount of acid gas which a solution will absorb may require higher than design circulating rates to avoid overloading of solution and consequent possibility of corrosion in transfer lines and exchangers. Another possibility for corrosion in heat exchangers exists as result of underestimating acid-gas partial pressure at a given solution loading so that, following point of pressure reduction, solution would be above its bubble-point temperature. It would release free hydrogen sulfide and carbon dioxide causing corrosion of mild steels. Tables, graphs.—INCO.           14151

### 8.4.3
**Blitzing Alkylation Problems. 3. How-To's on Reducing Corrosion.** L. RESEN. *Oil Gas J.,* **55,** No. 16, 116-117 (1957) April 22.

Problem of corrosion reduction in alkylation-fractionator was solved by a change in caustic strength, use of alloys, plastic linings and inhibitors. Corrosion took place slightly downstream of injection nozzle of unit reactors. Steel pipe and Monel linings would last only about 90 days in this service. A Saran-lined pipe eliminated this corrosion problem. After caustic was injected into effluent stream, it passed through 3 Duriron mixers. Pipe enclosing these was subject to corrosive attack and they were replaced by 2 Alloyco 20 globe valves. Corrosion inhibitors were used on the downstream fractionators. In caustic-wash system, corrosion of effluent pipe or nozzle was reduced by use of a Hastelloy tip welded to end of pipe to serve as nozzle. Diagrams.—INCO.     14163

### 8.4.3
**Corrosion Problems at Stanlow Refinery.** D. H. NICHOLSON. *Corrosion Prevention & Control,* **2,** No. 2, 37-39 (1956) Feb.

Methods adopted at Stanlow to combat corrosion include use of Epikote resin-base paints on pipes, vessels and equipment against atmospheric corrosion, sulfuric acid and caustic soda spillage, neutralization of hydrochloric acid formed in distillation processes, use of 2¼ chromium-1 molybdenum and 4-6 chromium-½ molybdenum steels for heater tubes to prevent hydrogen sulfide attack and molybdenum-bearing steels against naphthenic acid attack, addition of arsenic to brass for condenser tubes to prevent dezincification, the lining of pipes with bitumen and application of cathodic protection to prevent graphite softening of cast iron and dilution and washing of impurities to prevent formation of atomic hydrogen and blistering of steel. —INCO.                              13333

### 8.4.3
**What We've Learned in 20 Years About Gas Dehydrators.** W. SWERDLOFF. Paper before Gas Conditioning Conference, Univ. Okla. Norman, March 6, 1957. *Oil Gas J.,* **55,** No. 17, 122-129 (1957) April 29.

Report on process design and operation of glycol-absorption and solid-dessicant dehydration systems. Glycol system is superior to calcium chloride brine in that the pure solution is not corrosive and gives better drying. Glycol solutions have become the most common liquid dessicant for drying gas. During the last eight years, use of triethylene glycol instead of diethylene glycol has become widespread because of greater drying efficiency and increased resistance to decomposition. Glycol solution may become corrosive when impurities in the gas dry and cause problems in the dehydration unit. All precautions should be taken to keep air out of glycol solution. Presence of acidic components such as carbon dioxide and hydrogen sulfide will give further difficulties. Use of corrosion inhibitors is discussed. Hot solution corrodes at a greater rate than the cold solution most of the time. Corrosion because of carbon dioxide is magnified at higher pressures. Graphs, diagrams, tables.— INCO.                              14175

### 8.4.3, 4.3.5
**Stanolind Fights Corrosion in Three Sulfur Recovery Plants.** J. W. KILMER, M. H. RAHMES AND H. L. LAWLER. Paper before Natural Gas Assoc. Am. Ann. Mtg., Fort Worth, 1956. *Petroleum Refiner,* **35,** No. 7, 183-186 (1956) July; *Oil Gas J.,* **54,** No. 62, 84-85 (1956) July 9.

Principal cause of corrosion in three sulfur-recovery plants described is solution of corrosive gases in moisture condensed from process stream. Products of combustion penetrated openings in refractory lining of furnace and condensed on cool steel shell. Corrosion damage occurred to the stainless steel retaining flanges which in turn caused mechanical failure of the lead disk. Carbon steel and 304 stainless both failed in the sulfur tank cars and sulfur pit cover plates. Solution of problem was to redesign equipment so that contact of process stream with cold metal surfaces is minimized and externally insulate metal surfaces so that they do not cool to the water dew point of the process stream.—INCO.                   13887

# INDEX TO ADVERTISERS

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**8.4.3, 4.5.3**

**How Corrosion Attacks Well Casing.**
Y. W. TITTERINGTON. Corrosion Services,
Inc. *Oil Gas J.*, **55**, No. 21, 136-138, 140
(1957) May 27.

Corrosion of well casing is result of
either galvanic action, sulfate-reducing
bacteria or stray-current electrolysis.
Cathodic protection is a reliable and
useful method of protecting casing from
external corrosion. Current require-
ments are determined from either down-
hole potential-drop surveys or wellhead-
current-potential measurements. De-
scription of use of these methods is
given. Graphs, diagrams.—INCO. 14148

**8.4.3, 5.8.2**

**Preventing Corrosion by Crude: The
Use of Surface-Active Agents.** D. BASS.
Armour & Co. *Petroleum*, **20**, 139-142
(1957) April.

A review is given on the use of cat-
ionic surface-active agents, e.g., fatty
amines and their acetates, quaternary
ammonium compounds, etc., to combat
corrosion caused by crude oil both at
the oil well, particularly in water flood-
ing and at the refinery. 14212

**8.4.5**

**327 Basin Aluminum Corrosion Test.**
G. R. MALLETT. Hanford Atomic Prod-
ucts Operation. U. S. Atomic Energy
Comm. Pubn., HW-41370, Feb. 9, 1956,
8 pp. Available from Office of Technical
Services, Washington, D. C.

An investigation of corrosion in the
327 Building's water storage basin was
made to determine whether the static stor-
age of aluminum jacketed fuel elements
could cause corrosion effects that would
interfere with studies of in-pile corro-
sion. It was determined that the amount
and type of corrosion which occurs in
the 327 Building basin does not inter-
fere with the examination for aluminum
corrosion on irradiated slugs and that
the use of sodium nitrate as a corrosion
inhibitor was not necessary in the pre-
vention of excess aluminum corrosion
on slugs stored in the basin. (auth).—
NSA. 14107

**8.4.5**

**The Heavy Water Reactor for Power.**
W. B. LEWIS. Atomic Energy of Can-
ada Ltd., Chalk River Project, DL-25,
May 14, 1956, 52 pp.

The advantages of heavy water as
moderator and coolant in reactors for
economic power are mainly its negligi-
ble capture of neutrons and the ease of
maintaining it. It is shown that in com-
parison with sodium and ordinary water
as coolant, the saving in fuel costs can
more than offset the losses and interest
charges of the heavy water at the U. S.
price of $28/lb. Moreover, it is possible
to use natural uranium both as the
initial and make-up fuel. A further pos-
sibility is envisaged that a very long
irradiation of an artificial fuel, initially
$U^{235}$ + thorium, may prove economic
because of the reduction of processing
costs. Moreover on the $U^{233}$-thorium

cycle the use of heavy water may make
it possible to achieve a net gain from
breeding $U^{233}$. Against these advantages
must be set the necessity for controlling
loss not only on account of its cost but
also because of the ingestion hazard of
its rising content of $H^3$. Heavy water
enjoys the same advantages as ordinary
water of possessing good heat transfer
properties but also the disadvantage
that steam pressures become high at
relatively low temperatures. Both are
also chemically active at high tempera-
tures and attention must be paid to the
control of corrosion. The relative ad-
vantages of the pressurized tube and
pressure shell type of construction are
reviewed and a promising type of pres-
surized tube construction is suggested
that preserves good neutron economy.
The paper is mainly projected towards
very low power costs in which the total
of fuelling costs is less than 1 mill per
kwh. (auth)—NSA. 14031

**8.4.5, 1.6, 6.5, 4.7**

**Metallurgy Information Meeting,**
Ames Laboratory, Iowa State College,
May 2, 3 and 4, 1956. Ames Lab., Ames,
Iowa. U. S. Atomic Energy Comm.
Pubn., TID-7526 (Pt. 1), [1956], 284
pp. Available from Office of Technical
Services, Washington, D. C.

The topics included are: Nondestruc-
tive Testing of EBWR Fuel Plates,
Wetting Temperatures of Fuel Element
Components with Sodium and NaK,
Strengthening of Beryllium for High-
Temperature Use with Beryllium Oxide
and Beryllium Carbide Dispersion, Me-
chanical Metallurgy of Zircaloy-3B,
Mechanical Properties and Corrosion
Behavior of Zircaloy-3B, Constitution
of Uranium and the Platinum Metals,
Production of Thorium-Bismuth Disper-
sions, Preparation of Boron-Containing
Alloys, Aluminum-Boron and Alumi-
num-Uranium-Boron Alloys for Im-
proved Reactor Performance, Radio-
analysis of Krypton and Xenon and Its
Use in Diffusion Experiments with Sil-
ver, Preferred Orientation in Extruded
Thorium Rod, Morphology of Zirca-
loy-2, Microstructural Appearance and
Identification of Hydrides in Zirconium
and Zircaloy-2-Hydrogen Alloys, In-
spection of Small Diameter Tubing by
Eddy Current Methods, Application of
Immersed Ultrasonic Technique for the
Inspection of Small Diameter Tubes,
Corrosion and Mass Transfer by Lith-
ium at High Temperatures and Silicon-
izing of Metals in Liquid NaK.—NSA.
13947

**8.4.5, 3.5.8**

**Stress-Corrosion Cracking Problems
in the Homogeneous Reactor Test.** E.
G. BOHLMANN AND G. M. ADAMSON. Oak
Ridge Nat'l. Lab. U. S. Atomic Energy
Comm. Pubn., CF-57-1-143, January 31,
1957, 25 pp. Available from Office of
Technical Services, Washington, D. C.

Chloride-induced stress-corrosion
cracking has been encountered in the
homogeneous reactor test during the
preliminary testing. The reactor is con-
structed of austenitic stainless steels. It
is unique in that it will operate at 250
to 300 C with an aqueous uranyl sulfate
solution fuel containing 200 to 500 ppm
of dissolved oxygen. The cracking has
occurred in a secondary system used
for detecting leaks in the flanged joints
of the primary systems and in the
grooves of flanges in the primary sys-
tems. Tubing used in the leak-detection
system was found to be contaminated

with chloride introduced during manufacture. Examples of cracking of tubing and flanges are shown. In the laboratory it has been demonstrated that stress-corrosion cracking of austenitic stainless steels does not occur in oxygenated uranyl sulfate solutions unless chlorides are present. Results of the laboratory studies and studies in engineering loop experiments are discussed. (auth)—NSA.    13903

#### 8.4.5, 7.10, 3.7.3

**Metallurgical Examination of Resistance Thermometer Elements Removed from 105 KW and KE Areas.** L. A. HARTCORN. Hanford Atomic Products Operation. U. S. Atomic Energy Comm. Pubn., HW-37077, June 6, 1955 (Changed from Official Use Only January 23, 1957), 7 pp. Available from Office of Technical Services, Washington, D. C.

An examination was made of the resistance thermometer units which were removed from the KW and KE reactors. The examination was made in order to determine the extent of corrosion between the silver brazing alloy and the stainless steel nut and to establish that metallurgical defects exist in the brazes. Most of the elements from the KW reactor showed evidence of corrosion attack. The KE units had been installed with a rubber washer placed over the braze. Some of these units were corroded, but to a lesser degree than the KW units.—NSA.    13895

#### 8.4.5, 3.7.3

**Metallurgical Examination of Resistance Thermometer Elements: Rear Face 100-K and Prototype Units 100-H Areas.** LEWIS S. REED, L. A. HARTCORN AND W. R. SMITH. General Electric Company. U. S. Atomic Energy Comm. Pubn., HW-36210, April 18, 1955 (changed from Official Use Only January 23, 1957), 8 pp. Available from Office of Technical Services, Washington, D. C.

All the units which were examined after being in service only a short time exhibited some corrosion attack on the brazed joints and the brazed joints on the units which had been in service for periods up to a year were so extensively corroded that little or no braze metal remained. It is concluded from this examination that the silver brazing alloy used to make these units is not suitable for joining Type 416 stainless steel to Type 305 stainless steel in this service. (auth).—NSA.    14145

#### 8.4.5, 4.3.3

**Homogeneous Reactor Experiment Report for the Quarter Ending February 28, 1950.** C. E. WINTERS, editor. Oak Ridge National Lab., Tenn. U. S. Atomic Energy Comm. Pubn., ORNL-630, April 21, 1950 (Declassified January 13, 1956), 133 pp. Available from Office of Technical Services, Washington, D. C.

Solution Stability: Solution-stability experiments indicated that if the uranium sulfate solution is at a temperature of 65 C and at ORNL reactor flux, 1 to 2 excess molar sulfuric acid would be necessary to prevent precipitation of $UO_4$.

Corrosion: Short-term corrosion experiments at 250 C generally confirmed the selection of zirconium as the material of construction for the homogeneous reactor tank. The experiments also indicated that if too many liberties are taken with solution compositions, corrosion difficulties may be experienced. Stainless steels of a wide variety of

composition were generally attacked by uranyl sulfate at 250 C. Addition of extra sulfuric acid greatly accelerated the attack and, after a sufficiently long period of time in a sealed vessel, reducing conditions were set up with the resulting reduction of the uranyl ion to lower insoluble oxides, principally $U_3O_8$. Additions of oxidizing agents in moderate quantities in the form of hydrogen peroxide, nitric acid, and chromium trioxide to the vessels stopped the uranyl reduction and reduced the attack on the stainless steel to tolerable values. Unfortunately, one series of experiments with uranyl sulfate plus stabilized nitric acid, with or without excess sulfuric acid showed a very serious form of intergranular type of attack on zirconium. A single experiment with chromium trioxide did not produce this type of attack. Over-all, it continues to appear that there are several conditions under which a uranyl sulfate homogeneous reactor is feasible. Operation is possible at 250 C with uranyl sulfate without excess acid, using a zirconium tank and with the external system constructed of zirconium and perhaps titanium or certain of the precious metals. Operation is possible at 100 C, using a wide variety of materials of construction, including stainless steel, if sufficient excess acid is incorporated in the solution to prevent precipitation.

Physics: Aside from minor dimensional corrections to conform to mechanical design values, the calculations of critical mass are complete and indicate a favorable assembly. The question of shimming and of safety and regulating rods is still incomplete.

Engineering and Design: Preliminary designs are given for the reactor and auxiliaries. A program is reported to design and construct a non-nuclear model to demonstrate the feasibility of operating at 1000 psi and 250 C. (auth) —NSA.    13936

#### 8.4.5, 6.2.3

**Investigation of Unclad Carbon Steel for Pressurizer Applications.** PAUL E. BROWN AND KURT KATZ Atomic Energy Div., Westinghouse Electric Corp. U. S. Atomic Energy Comm. Pubn., WAPD-A1W(PCh)-46, January 25, 1956, 60 pp.

Bound with this report with separate pagination is: Examination of Carbon Steel Pressurizers. C. F. Paulson. WAPD-A1W(PCh)-55, [n. d.], 3 pp.

Unclad carbon steel for use in the A1W pressurizer was studied in the liquid, alternate liquid and vapor and vapor phases using air and steam start-ups. Air caused serious corrosion but no excessive corrosion was caused by steam. The presence of ammonia reduces the liquid phase corrosion rate but does not affect the corrosion rate in the other phases. Oxygen concentrations of 2 to 6 cc/kg of water are tolerable for steam pressure start-ups.—NSA.    13944

#### 8.4.3, 4.6.4

**Tidewater's Delaware Refinery.** *Oil Gas J.,* 55, No. 21, 159-198 (1957) May 27. Papers include: This Refinery Didn't Grow, J. P. O'Donnell; Flexibility is Designed Into the Crude Unit, W. E. Colburn; The Fluid Coker, J. A. Whitcombe; The Fluid Catalytic Cracker, J. M. Phelps; The Gas Plant, H. A. Baird; The Polymerization Unit, S. H. Dyer; The Alkylation Unit, S. R. Stiles and H. A. Baird; The Houdriformer Unit, H. W. Day; The Desulfurizer Unit, H. W. Day; The Hydrogen Plant,

J. V. Class; The Sulfur Plant, J. M. Phelps; Gasoline, Fuel Blending, R. N. Wimpress; Instrumentation, W. C. Gardner and J. E. Leary; Automation Pacemaker; Cooling Water, H. P. Evans and E. E. Elliott; The Marine Terminal, D. J. Dobbs and J. M. Phelps; The Maintenance Program.

Description of Tidewater's new Delaware refinery. An extensive variety of special materials provides for corrosion protection. Ammonia helps to protect top section of gasoline column, atmospheric column and each stage of ejector system of vacuum column of crude unit. Kontol affords protection to overhead duct from atmospheric column and ducts of vacuum column ejector system. Monel provides protection in top of gasoline column, overhead line, condenser shells, foul-condensate pumps and of top ⅔rds of the gasoline stabilizer column. Inconel protects bottom third of stabilizer, reboiler lines and shellside. Lining and internals of Type 316 stainless protect part of light-gas-oil stripper. Other uses of this same material include transfer lines between fired heaters and columns. Chromium steels are used for fired heater tubes and hot process lines. In gas plant, corrosion inhibitor is injected in hydrogen sulfide removal section to inhibitor corrosion from acid gas. Piping throughout reformer unit is of steel. Main exception is hydrogen service above 500 F where materials are usually 1 chromium-½ molybdenum for piping, exchangers and reactor shells. Heater coils are 2¼ chromium-1 molybdenum. Alloys protect against corrosion of tubeside parts of coolers and condensers in contact with salt water. Effluent piping from reformers is fabricated of Incoloy because of high temperatures encountered. Corrosion by moist carbon dioxide is minimized in critical equipment locations by use of aluminum and Monel. Piers of marine terminal are double decked structures of reinforced-concrete slabs supported on H-section steel piles. Photos, diagrams.—INCO.    14180

#### 8.4.5, 4.3.5, 4.7

**A Study of Nitrogen as a Cover Gas in Sodium Systems (Technical Report No. 53).** E. F. BATUTIS, C. A. PALLADINO, R. GAGNE AND J. W. MAUSTELLER. Mine Safety Appliances Co., Callery, Pennsylvania (Contract NObs-65426), Dec. 7, 1956, 25 pp.

Nitrogen used as a cover gas in several MSA sodium systems, ranging from 900 to 1100 F and 1 to 7 fps, did not induce excessive corrosion of Types 304 and 347 stainless steel and tool steel specimens. Average corrosion rates found of the stainless steels ranged from $+0.01$ to $+0.23$ mg/cm²-mo and tool steel ranged from $-0.24$ to $-0.96$ mg/cm²-mo. The corrosion rate of beryllium in a 1100 F sodium system (S2G mock-up) for six specimens exposed for 90 days averaged 1.27 mg/cm²-mo. This rate of beryllium attack may be undesirable in some applications and would require definite consideration in design work. Factors affecting beryllium attack to varied degrees were: entrained nitrogen, calcium content, temperature and distance to sodium-nitrogen interface. The order of magnitude of these factors was not definite but the last mentioned seemed to be least effective. These factors were negligible in the corrosion of stainless steels and tool steel in the MSA test systems. (auth) —NSA.    13881

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ol. 14

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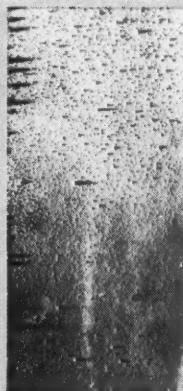
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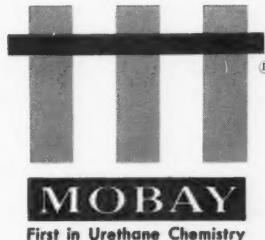
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